SORPTION AND DEGRADATION PARAMETERS FOR MODELING NEMATICIDE FATE IN SOIL

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ABSTRACT

Since the ban of the traditional fumigants, DBCP and EDB, for nematode control in pineapple, there has been considerable interest in a non-volatile organosphosphorus nematicide, fenamiphos [Nemacur®, ethyl 3-methyl-4-(methylthio)phenyl (1-methylethyl) phosphoramidate]. The fate of fenamiphos is unknown in diverse field soils in Hawaii. The ability of mathematical simulation models to predict movement and persistence of fenamiphos in soils from key input parameters associated with mathematical descriptions of degradation, sorption and leaching, will aid us in designing optimum management strategies to achieve maximum efficacy and minimize environmental contamination. In view of the proposed modeling efforts, experiments were conducted to evaluate the errors and uncertainties in measurements of two important processes, sorption and degradation.

Fenamiphos sorption measurements were conducted by the conventional batch method on Molokai and Pane soils under aerobic conditions. The impact on measured sorption by (1) degradation of fenamiphos during equilibration, (2) variable moisture status of soils before measurements and (3) equilibration time were evaluated. Apparent sorption and sorption corrected for degradation at both 4 and 24 hours equilibration on both soils increased in the following order: field-moist < prewetted < air-dried. Degradation of fenamiphos to fen. sulfoxide during batch equilibration occured at all moisture treatments, and the impact of degradation (45% of fenamiphos degraded) on sorption measurement was significant on the Pane soil. On the Molokai soil however, the impact was negligible because less than 20% of fenamiphos degraded. Competition of water molecules with fenamiphos for sorption sites and fenamiphos degradation during equilibration probably accounted for the differences in sorption due to pre-sorption moisture status. The percentage differences in fenamiphos sorption between air-dried and field-moist soils after 24 hours equilibration were 34 % and 37% for Pane and Molokai soils, respectively. The effect of initial moisture on sorption measurements may not be of practical importance when we consider that the average coefficient of variation of fenamiphos and fen. sulfoxide sorption determined on soils obtained from nine fields was 35% and 46%, respectively.

In the degradation study, the reliability of using laboratory-generated degradation rates for fenamiphos and fen. sulfoxide to predict degradation of these nematicides under field conditions was evaluated. Field and laboratory methods of determining fenamiphos degradation were compared at six locations within two cropped pineapple fields on the Oahu Dole and Del Monte plantations; the methods were compared using first-order degradation rates and the quantity of fenamiphos residue remaining at a given time. A similar comparison with fen. sulfoxide was performed on the Del Monte field. In field experiments, nematicides were applied to insitu field cores contained in aluminum cylinders (inserted into the tilled layer of pineapple beds) at six locations per field. Laboratory experiments were performed by application of 14C-labeled nematicides to soils collected from the same locations as the field tests; treated soils were incubated under controlled temperature and moisture. On the Del Monte field, the field and laboratory degradation data were fit reasonably well by first-order kinetics. First-order degradation rates determined from laboratory and field methods were similar. Fenamiphos degradation data from the Dole field generally deviated statistically from first-order kinetics; the better statistical resolution of deviations from first-order kinetics on the Dole field was largely due to a much lower overall standard error for this field. The difference, however, between laboratory and field measured fenamiphos residues on the Dole field was within a factor of 1.4. In view of the uncertainties in degradation measurements contributed from field soil variability and analytical techniques, this differrence is tolerable. Degradation rates of fenamiphos and fen. sulfoxide determined from laboratory methods are therefore considered reliable estimates for modeling persistence of these chemicals in field soils under pineapple cultivation.

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CHAPTER I

GENERAL INTRODUCTION

GENERAL INTRODUCTION

Chemical control of nematodes is crucial to the economic survival of the pineapple crop in Hawaii. The most effective chemicals used in the pineapple industry were the fumigants, DBCP and EDB. The detection of these fumigants in groundwaters in various states (including Hawaii on Oahu and Maui) led to the inevitable ban of these chemicals. While it is debatable as to the sources of the contamination in Hawaii, fumigant use in pineapple fields for decades is a prime suspect.

A viable alternative for chemical control of nematodes is a non-volatile organophosphorus nematicide, fenamiphos [Nemacur®, ethyl 3-methyl-4-(methylthio) phenyl (1-methylethyl) phosphoramidate]. It has considerable potential because it is effective against reniform nematodes at low doses and can be applied (elmulsifiable formulation) with irrigation water through the drip irrigation system for timed application throughout the cropping cycle. An earlier laboratory study (Lee et al., 1986) found that fenamiphos is very rapidly degraded (half-life = 3 days) by oxidation and moderately sorbed to soils (K_f = 4.5 ml g^{-1}). The major metabolite, fenamiphos sulfoxide persists much longer (half-life = 80 days) and being more polar is sorbed much less (K_f = 1.2 ml g^{-1}) than fenamiphos. Fenamiphos has been reported to control nematodes for 4 to 12 weeks (Homeyer and Wagner, 1982; Johnson, 1982). Considering the short persistence of fenamiphos, the residual effects can be largely attributed to the persistence of fen. sulfoxide. Fen. sulfoxide is subject to slow oxidation to fenamiphos sulfone (half-life =16.4 days) and/or hydrolyzed to fenamiphos sulfoxide phenol. Fenamiphos and fen. sulfone are also susceptible to hydrolysis to fen. phenol and fen. sulfone phenol, respectively; the phenols are considerably less toxic than the nematicidally active fenamiphos, fen. sulfoxide and fen. sulfone. In a 56-day laboratory incubation study by Ou and Rao (1986), it was found that the half-life of fenamiphos was < 3 days in an Arredonda sandy soil (Grossarenic Paleudult) but the half-life of the total toxic residue (fenamiphos, fen. sulfoxide and fen. sulfone) ranged from 38 to 67 days. In this study, fen. sulfoxide phenol accounted for <15% of the total applied radioactivity.

Fen. phenol was never detected while fen. sulfone phenol appeared only at 56 days.

In field experiments where fenamiphos was applied either through overhead sprinklers or broadcast in granular form on a Lakehead sandy soil from Tifton, Georgia (Johnson et al., 1982), the half-life of the total toxic residue (TTR) was estimated to be 14 days. Fenamiphos half-lives in the range of 4 to 5.7 days were measured in a sandy soil (San Francisco, California) cultivated with turfgrass which was previously treated with granular fenamiphos; only trace amounts of TTR remained after two weeks (Peterson et al., 1986).

Little is known of the behavior of fenamiphos in different field soil environments in Hawaii. If we are to make wise management decisions regarding the use of this chemical for maximum protection of both crops and the environment, we urgently need a thorough understanding of the complex interactions of the chemical, soils, plant and the environment. The principal processes involved include (a) degradation (mediated by chemical and/or microbial processes), (b) sorption and desorption, (c) leaching and (d) plant uptake. These processes are in turn profoundly affected by environmental factors such as temperature and moisture.

A valuable tool that can aid in such management decisions is simulation modeling. Mathematical simulation models are powerful tools that have the capability of forecasting pesticide mobility and persistence in different soil environments from key input parameters associated with mathematical descriptions of degradation, sorption, and leaching. Climate and management variables (irrigation, frequency and amount of application) can be incorporated by way of specified boundary conditions. Although it is not feasible to conduct field experiments on pesticide dissipation at all field locations of interest, the impact of a multitude of soil, crop, climatic and management combinations can be simulated.

The success of using simulation models at the field-scale, according to Rao and Jessup (1982), is largely dependent upon the limitations imposed by uncertainties (or errors) in three crucial areas:

(1) model input parameters (measured from laboratory or field experiments),

(2) model output data (generated from mathematical calculations of the simulation models),

(3) field-measured pesticide residues (commonly used for model output comparisons or verification).

Since models are currently used for predicting pesticide behavior in diverse field soil environments, and will certainly gain increasing importance in the near future, it is imperative that we carefully evaluate the reliability of model input parameters for simulation purposes. The magnitude of errors associated with measurements of key input parameters and model output data must be compared realistically with the magnitude of uncertainties encountered in field-measured pesticide residues. Thus, if the variability of field residue levels used to evaluate model performance is large, then attempts to achieve high precision and accuracy in parameter measurement may not be warranted.

Input parameters associated with sorption and degradation are generally measured in the laboratory for reasons of convenience and greater control of variables by the researcher. Furthermore, accurate characterization of degradation in the field is difficult and usually more variable because of soil spatial and temporal variability (chemical, biological and physical properties) and management variables (mode of application and tillage). Error estimates associated with the sorption or degradation parameters and statistical analyses of the data are seriously lacking in the literature. Since laboratory data sets will inevitably be used by numerous investigators for mathematical modeling, more rigorous quality control methods must be enforced to aid in evaluating the reliability of the data sets for modeling field behavior of pesticides.

The overall objectives of this study are (a) to evaluate the uncertainties in laboratory measurements of input parameters associated with two important processes, sorption and degradation, and (b) to assess the reliability of using laboratory-determined degradation data for prediction of field persistence. Not included in this study is the assessment of uncertainty in model output data. In sorption experiments, the error introduced in measuring fenamiphos sorption on airdry soil (versus "field-moist" soil) was evaluated. The magnitude of the error was evaluated in the context of the variability expected in sorption measurements on soil samples from numerous field locations in large fields. In degradation experiments, degradation rates for fenamiphos and fen. sulfoxide nematicides were measured at several locations in two fields on Oahu and in the laboratory on soils collected from the

field. Comparisons of laboratory and field degradation rates were based on first-order kinetics and actual amount of nematicide remaining at specific time intervals. Chapters 2 and 3 represent highlights of the sorption and degradation studies, respectively. As they are written in a format suitable for journal publication, additional details of the experiments are provided in the appendices.

CHAPTER II

SORPTION

INFLUENCE OF INITIAL MOISTURE AND DEGRADATION ON SORPTION OF FENAMIPHOS NEMATICIDE IN SOILS

INTRODUCTION

Errors in Laboratory Sorption Measurements - Soil Moisture, Sterilization, and Equilibrium Time

Sorption of organic chemicals on soils is usually measured by the conventional batch-slurry method. Large errors in sorption measurements can be introduced when soils are subjected to a variety of experimental conditions such as variable solution:soil ratios, ionic strength of aqueous solution and soil pretreatments like air-drying and sterilization. Since sorption data are increasingly used in mathematical simulation models for assessment of environmental fate of organic chemicals, the errors associated with generating sorption data in the laboratory must be critically evaluated with regard to the inherent sorption variability encountered in the field.

The standard EPA protocol (USEPA, 1978) for measuring pesticide sorption on soils recommends that air-dried soils be used, but for sediments the natural wet condition is preferred (Mill et al., 1981). There is sufficient evidence to show that water molecules associated with soil surfaces (both mineral and organic) compete effectively with pesticide molecules for sorption sites, resulting in a reduction in the sorptive capacity in moist as compared with previously air-dried soils. The wide range of pesticides reported to exhibit this phenomenon includes disulfoton (Graham-Bryce, 1967), parathion (Yaron and Saltzman,1972), atraton and monuron (Hance,1977), atrazine (Dao and Lavy, 1978), and DBCP (Liu et al., 1983). There is also indirect evidence from biological data to demonstrate that efficacy of pesticides can be greatly reduced when applied to soils at low rather than high soil moisture contents (Upchurch, 1957; Hollist and Foy, 1971; Swann and Behrens, 1972; Okafor, et al., 1983). All of the authors attributed the lowered efficacy to increased sorption in dry soils associated with reduced effective pesticide concentration in solution against target organisms. If fate assessments are performed on agricultural soils that are usually in a relatively moist condition in the field, then it may be prudent to measure sorption on moist soil samples.

Sorption measurements however, are further complicated if rapid microbial and/or chemical degradation of the parent chemical occurs during batch equilibration. Reduction of degradation losses during sorption experiments can be accomplished by using, (1) sterilization techniques both chemical and physical (e.g. autoclaving and irradiation), (2) anaerobic conditions for compounds which degrade only under aerobic conditions, (3) initially air-dried soils and (4) short (< 4 hours) equilibration times. While some of the above techniques may minimize or eliminate degradation, additional errors, related to alteration of the delicate physico-chemical properties of the soil-system, can be readily introduced. For instance, Dao et al. (1982), demonstrated that autoclaving soils under intense heat and pressure decreased the sorption of both aniline and diuron by at least two fold. In adsorption experiments with 2,3-diclorophenol and 2,4-diclorophenol, Boyd and King (1984) showed a significantly higher Freundlich coefficient (K_f) for autoclaved than air-dried soils. Co-60 irradiation of soils was found to enhance chemical oxidation of fenamiphos, resulting in a reduction of the linear sorption coefficient (K_d) by a factor of two (Cheng-Tseu, et al.,1987). Anaerobic conditions, such as imposed by an N_2 atmosphere, were used to quantify sorption of p-cresol (Boyd and King, 1984) and 2,4,5-T (Koskinen and Cheng, 1982). It should be pointed out however, that for certain combinations of organic chemicals and soil types, anaerobic degradation may also introduce errors in sorption measurements. Since aerobic conditions are present in most surface soil systems, it may be wise to conduct sorption of organic chemicals under similar conditions in the laboratory, even though the chemical may be readily degradable (labile). The errors in sorption measurements under favorable degradation conditions may or may not be larger than those introduced by various techniques used to reduce degradation.

If initially air-dried soils and short equilibration times (<4 hours) are used one risks not attaining equilibrium (Dao et al., 1982; Felsot and Dahm, 1979; Green and Corey, 1971; Hance, 1967). Moreover, depending on the sorptive capacity of the soil and stability of the organic compound, there is no guarantee that the effect of degradation is negligible unless the actual amount of the parent chemical is extracted from the soil and solution phases in the sorption measurement procedure. The general use of air-dried soils is likely the result of the convenience of handling, sieving and

storing air-dried soils rather than a strategy for attenuating microbial activity and the associated breakdown of organic sorbates. Air-drying of soils prior to sorption measurements may in fact retard sorbate degradation, at least when brief equilibration periods are employed. In a study in which air-dried soil was preincubated with water for three days prior to measurements of phenol sorption, Scott et al. (1982) attributed the rapid increase in apparent sorption on preincubated over air-dried soils to the greater microbial population capabie of degrading phenol. If longer equilibration time periods (>12 hours) are used, degradation will surely occur for labile organic chemicals. However, various methods (which themselves are subject to errors), can be employed to correct for degradation, assuming that the actual amount of the parent chemical in both soil and solution is known (Koskinen and Cheng, 1982).

The focus of this chapter is to critically evaluate the difficulties and associated errors involved in measuring sorption of a labile nematicide, fenamiphos, on soils at various moisture contents under aerobic conditions. Since the laboratory generated sorption data will be used in simulation models to assess the fate of fenamiphos under diverse soil-types, the acceptability of the error from laboratory experiments will be weighed against the uncertainties in sorption variability encountered at the field scale.

MATERIALS AND METHODS

Surface soils (0-15 cm) were collected from two field which were under pineapple cultivation and had no previous fenamiphos application. The soils were Molokai silty clay loam (Typic Torrox) and Pane silt loam (Typic Dystrandept). Physico-chemical properties for Molokai soil includes organic carbon (1.2%), pH (5.8), CEC (20 meq/100g) and for the Pane soil; organic carbon (4.5%), pH (5.4), CEC (54 meq/100g). Aqueous fenamiphos solutions with a range of concentration from 1.5 to 30 ug/ml were made from a mixture of fenamiphos-ring-1-14C (>95% pure) and analytical grade fenamiphos (>97% pure). The three moisture treatments used in the sorption experiments were, (1) field moist: fresh samples from the field were brought in the laboratory and immediately passed through a 2 mm sieve, and then stored in plastic bags for no longer than two weeks at ambient (23°C) laboratory conditions prior to sorption measurements, (2) air-dried: field moist samples were air dried at 25°C and 70% relative humdity in the laboratory for two days and (3) prewetted: previously air-dried samples were wetted to the original field moisture content and incubated for two days before sorption measurements. The air-dried and field-moist moisture contents were 16.7% and 30.4%, for the Pane soil, and 5.2% and 25.2% for the Molokai soil. Samples equivalent to 2.0 g oven-dried soil were weighed into 30 ml glass tubes (Corex), and 10 ml of the appropriate nematicide solution were added to yield a 5:1 solution:soil ratio (see schematic for experimental procedure, fig. 1). The tubes were sealed with aluminum-lined stoppers and shaken on an end-over-end rotary shaker (Cole-Parmer) for 4 or 24 hours at 23°C ± 2°C. After batch equilibration, the samples were centrifuged for 50 mins at 17,000 g and duplicate aliquots (0.5 ml) of the supernatant were mixed with 5 ml of scintillation cocktail (Aquasol) in filmware tubes (Nalgene) and radioassayed using liquid scintillation techniques (Packard 4000). Samples of fenamiphos solution without soil were used as standards. Since there was negligible loss of the nematicide due to tube adsorption and/or volatilization, the difference between the radioactivity of the standard and the supernatant was assumed to be due to fenamiphos sorption on soil.

The amount of fenamiphos and the major metabolite, fenamiphos sulfoxide remaining in both solution and soil phases after equilibration was determined by first

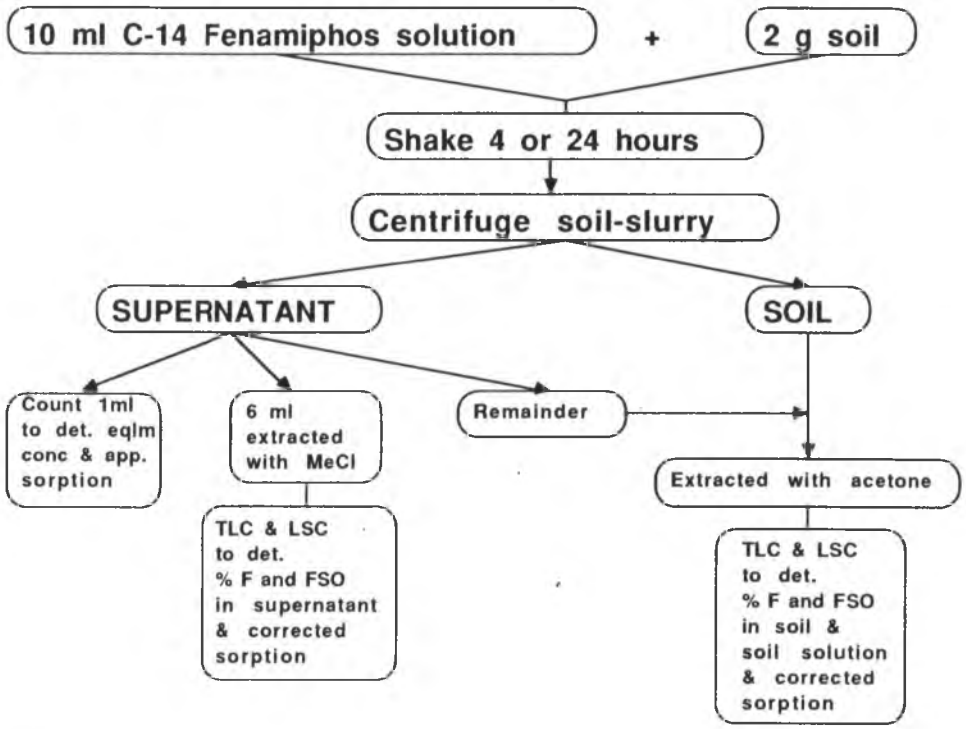

Figure 1 Schematic of sorption experiment

extracting 8 ml of the supernatant solution with 10 ml of methylene chloride for three times on a rapid Mixxor separatory system (Cole Parmer). Five strokes of the piston are equivalent to approximately 40 shakes of a conventional separatory funnel. The remainder (i.e. 2 ml soil solution with 2.0 g soil) was further extracted twice with 200 ml acetone on a wrist-action shaker for 30 min. Both concentrated methylene chloride and acetone extracts were then separately subjected to thin-layer chromatography and radioassayed (Cheng-Tseu et al., 1987).

The sorption data were fitted to the log form of the Freundlich model,

$$\log S = \log K_f + N \log C \qquad [1]$$

(where S = μg sorbed nematicide/g soil; C = μg nematicide/ml solution after equilibration; K_f = Freundlich sorption coefficient; N = constant related to the linearity of the isotherm). Apparent sorption data were those generated from conventional calculations. Corrected sorption data however, were calculated from the actual amount extracted from both the soil and supernatant phases. Other statistical analyses include comparison of slopes and elevations (intercepts) of the best-fit regression lines and calculation of 95% confidence intervals for the intercepts (K_f) and slope (N) from the standard errors of the estimates and the appropriate t-test (Dao et al., 1982).

RESULTS AND DISCUSSION

The influence of pre-equilibration soil moisture regime on fenamiphos sorption on two soils at two equilibration times is shown in figures 2 and 3. Both apparent and corrected sorption data can be adequately described by the Freundlich equation (r^2>0.95, P = 0.01); K_f and N values and their associated 95% confidence limits for both Molokai and Pane soils are presented in tables 1 and 2. Generally, airdrying soils increased apparent and corrected sorption at both 4 and 24 hours equilibration by 1.4 fold in the following order: air-dried > prewetted > field-moist. The observation that field-moist and prewetted soils effectively sorbed less fenamiphos than air-dried soils implies that (1) moisture closely associated with soil particles may be a strong competitor with fenamiphos for sorption sites, (2) degradation may be accelerated in favorable moist soils or (3) "true" equilibrium may be different for each moisture treatment and may or may not be attained at the two equilibrium times. The effect of these three important factors, moisture, degradation, and equilibrium time on apparent sorption will be discussed in detail for each soil.

Pane Soil

Apparent fenamiphos sorption declined by a factor of 1.2 for all moisture treatments after 24 hours equilibration. The degradation data showed that after 24 hours an average of 45 % of fenamiphos from the soil and solution phases had degraded to the major metabolite, fen. sulfoxide. Since fen. sulfoxide is sorbed at least four times less than fenamiphos (Lee et al. 1986), it is evident that the lower apparent sorption must be attributed to the formation of the polar metabolite, fen. sulfoxide. Sorption coefficients for fen. sulfoxide ranging from 1.4 to 1.9 were calculated from the amounts extracted from the soil and solution phases after 24 hours equilibration (table 1). The smaller fen. sulfoxide K_f confirms the lower affinity of this metabolite for soil surfaces and is also comparable to a K_f value of 1.2 determined for fen. sulfoxide from previous sorption studies (Lee et al.,1986). Researchers working with similar labile organic chemicals which possess a readily oxidizable sulphide group (eg. phorate, aldicarb, terbufos, disulfoton and fenthion) must thus be forewarned that a measured apparent sorption could consist of a substantial amount of the polar metabolite.

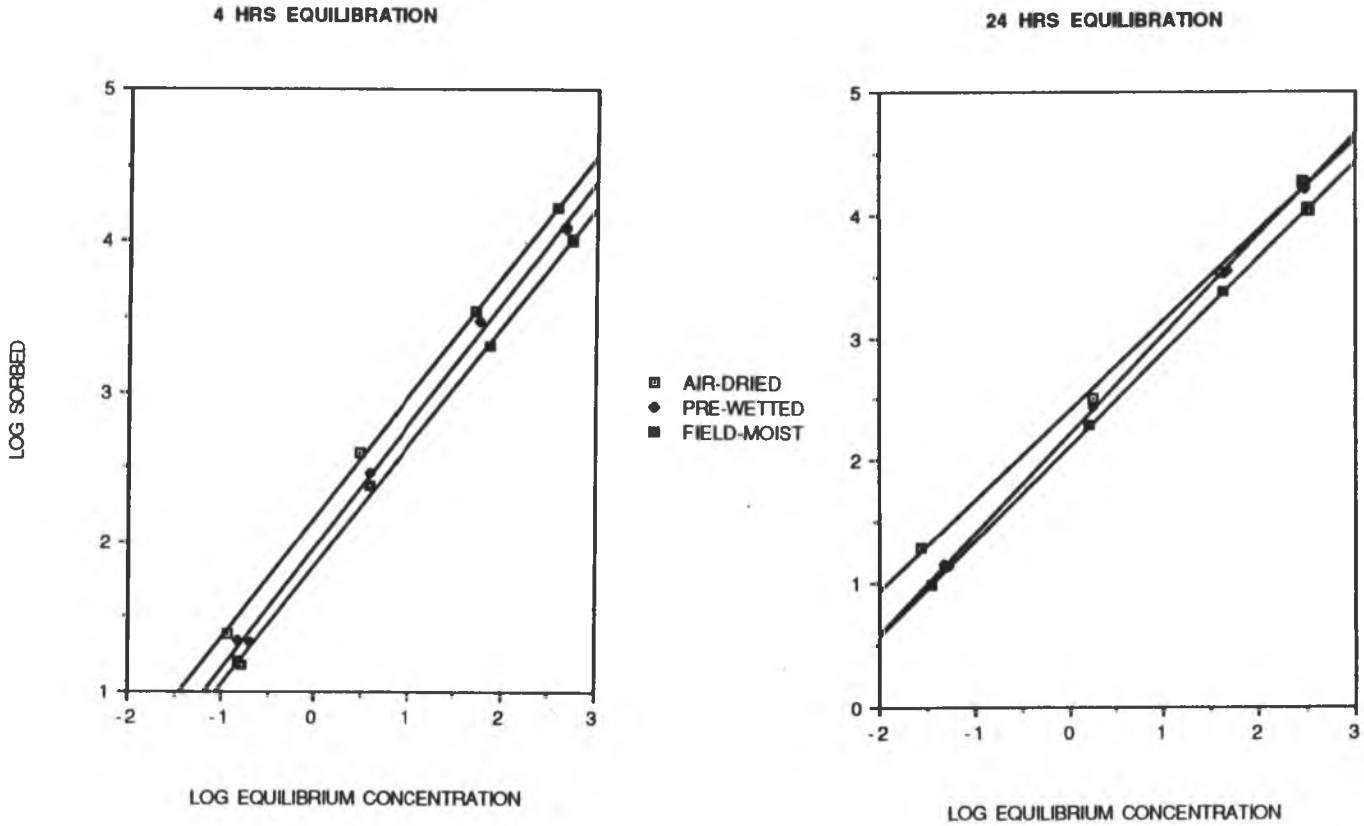

Figure 2 Effect of initial soil moisture content and two equilibration times on corrected sorption of fenamiphos on Pane soil. Equilibrium concentration = ug/ml and sorbed phase = ug/g soil

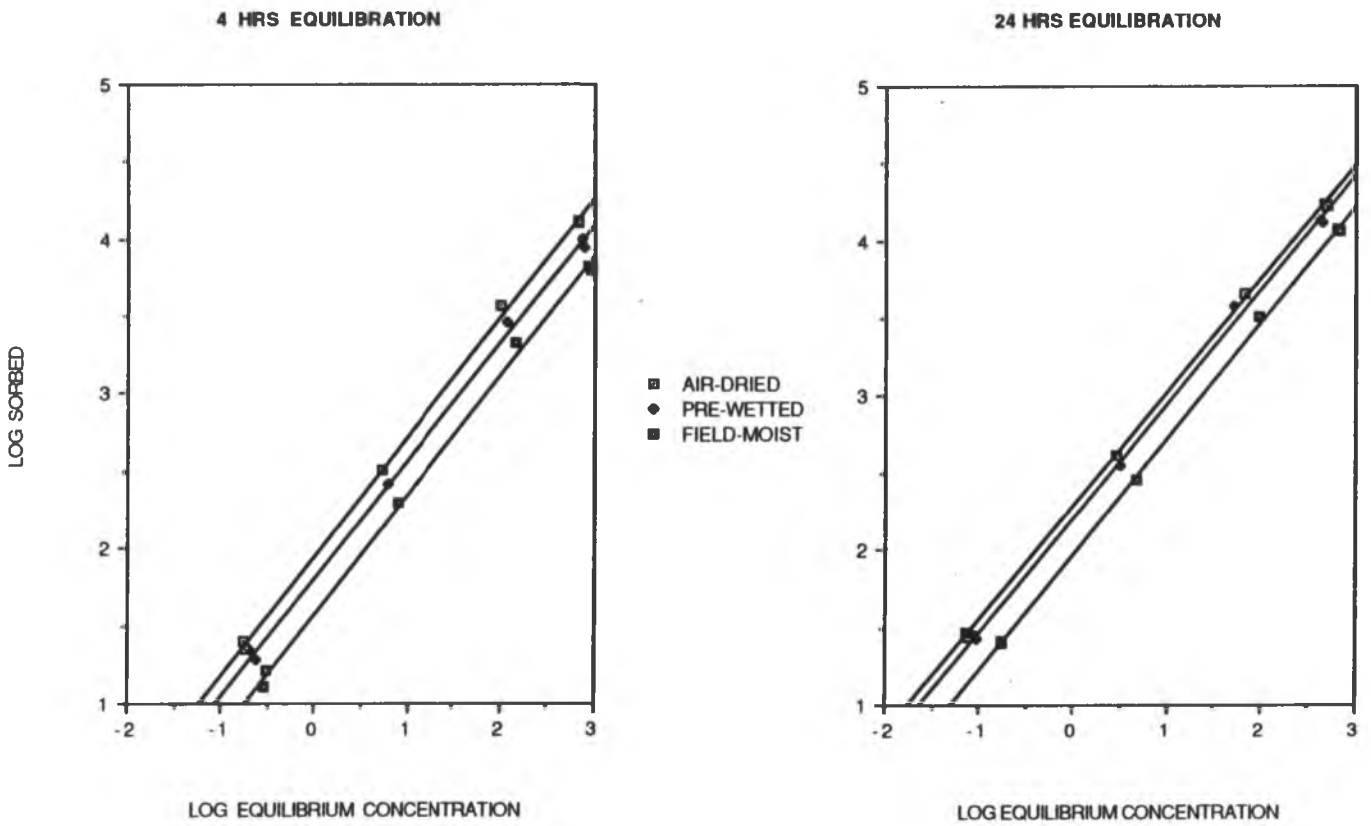

Figure 3 Effect of initial soil moisture content and two equilibration times on corrected sorption of fenamiphos on Molokai soil. Equilibrium concentration = ug/ml and sorbed phase = ug/g soil

Table 1 Sorption Coefficients and Isotherm Slopes for Fenamiphos and Fen. Sulfoxide on Pane Soil

Chemical	Time (Hours)	Moisture Treatment *	Isotherm Coefficients§			
			K_f**		N	
			Apparent	Corrected	Apparent	Corrected
Fenamiphos	4	AD	8.13 (7.68-8.59)	8.71 (8.22-9.22)	0.83(±.03)	0.77(±.03)
	4	PW	6.82 (6.46-7.20)	7.15(6.55-7.81)	0.84(±.03)	0.81(±.05)
	4	FM	5.84 (5.40-6.33)	6.36(6.00-6.75)	0.83(±.04)	0.79(±.03)
	24	AD	6.79 (6.23-7.40)	11.13(10.26-12.07)	0.92(±.05)	0.74(±.05)
	24	PW	6.06 (5.62-6.54)	9.13(8.84-9.42)	0.95(±.04)	0.82(±.02)
	24	FM	4.65 (3.92-5.52)	8.33(8.12-8.55)	0.97(±.03)	0.77(±.01)
F. Sulfoxide	24	AD		1.59(1.09-2.32)		1.12(±.52)
	24	PW		1.91(1.31-2.79)		1.02(±.46)
	24	FM		1.44(0.96-2.16)		1.23(±.46)

* AD - airdried
PW - prewetted
FM - fieldmoist

** K_f units are in ml g^{-1}

§ numbers in parenthesis are the 95% confidence interval. Confidence intervals for K_f are the antilogs of log $K_f \pm t \times SE(\log K_f)$ where t = student's t-value and $SE(\log K_f)$ = standard error of log K_f

Table 2 Sorption Coefficients and Slopes of Fenamiphos on Molokai Soil

Chemical	Time (Hours)	Moisture* Treatment	Isotherm Coefficients§			
			K_f**		N	
			Apparent	Corrected	Apparent	Corrected
Fenamiphos	4	AD	7.34 (6.93-7.76)	7.06(6.66-7.49)	0.76(±.03)	0.77(±.03)
	4	PW	6.35 (5.95-6.78)	6.13(5.68-6.63)	0.76(±.03)	0.76(±.04)
	4	FM	5.35 (4.99-5.74)	4.86(4.38-5.38)	0.77(±.04)	0.77(±.05)
	24	AD	9.22 (8.74-9.72)	9.89(9.54-10.26)	0.77(±.03)	0.73(±.02)
	24	PW	8.61 (7.77-9.54)	8.86(8.15-9.63)	0.76(±.06)	0.73(±.05)
	24	FM	7.47 (6.98-8.00)	7.24(6.90-7.59)	0.75(±.04)	0.75(±.03)

* AD - airdried
PW - prewetted
FM - fieldmoist

** K_f units are ml g^{-1}

§ numbers in parenthesis are the 95% confidence interval. Confidence intervals for K_f are the antilogs of log $K_f \pm t \times SE(\log K_f)$ where t = student's t-value and $SE(\log K_f)$ = standard error of log K_f

When the sorption data were corrected for degradation, there was no significant change in the 4 hour equilibration data but a 1.6 fold increase in K_f was found in the 24 hour equilibration treatment. Note also that the isotherm slopes (N) did not change substantially with correction for degradation for the 4 hour equilibration treatment but decreased significantly by a factor of 1.3 for the 24 hour treatment. The small amount of fenamiphos degradation (average of 18 % of fenamiphos degradation for all moisture treatments) after 4 hours equilibration and the variability contributed from experimental error may account for the homogeneity of slopes and sorption coefficients even after correction for fenamiphos degradation. For the 24 hours equilibration treatment however, the amount of fenamiphos degradation was concentration dependent; initial concentrations of 30 µg/ml and 1.5 µg/ml corresponded to 14% and 40% fenamiphos degradation, respectively (fig. 4). Because of the accelerated degradation at lower concentration, the overall effect of the corrected sorption isotherm was a decreased slope (N) i.e. higher sorption at the lower equilibrium concentrations (fig. 5). The large amount of fenamiphos degradation to fen. sulfoxide therefore explains the significant increase in K_f after correction for degradation. Although most pesticide degradation studies (Hamaker, 1972; Altom and Stritzker, 1973; Parker and Doxtader,1982) demonstrate a decline in degradation rate with increasing concentration, only a few studies show this effect in sorption experiments. In experiments of phenol adsorption on two soils, Scott et al.(1982) confirmed that microbial degradation of phenol was inhibited as the concentration of phenol increased from 10^{-5}M to 10^{-2}M. Koskinen (1984), however, cautioned against any emphasis on the effect of initial concentration on the degradation rate because of the low actual amounts of degradation product (DCPMU) measured; only 19% of the parent chemicaL, methazole, degraded.

There was a general trend of increased fenamiphos degradation at field-moist as compared with either prewetted or air-dried conditions after 24 hours equilibration; at least an increase of 5% and 10% in fenamiphos degradation was detected at fenamiphos initial concentrations of 30 and 1.5 µg/ml, respectively (fig. 4). The increase in fenamiphos degradation is likely due to a larger microbial biomass present

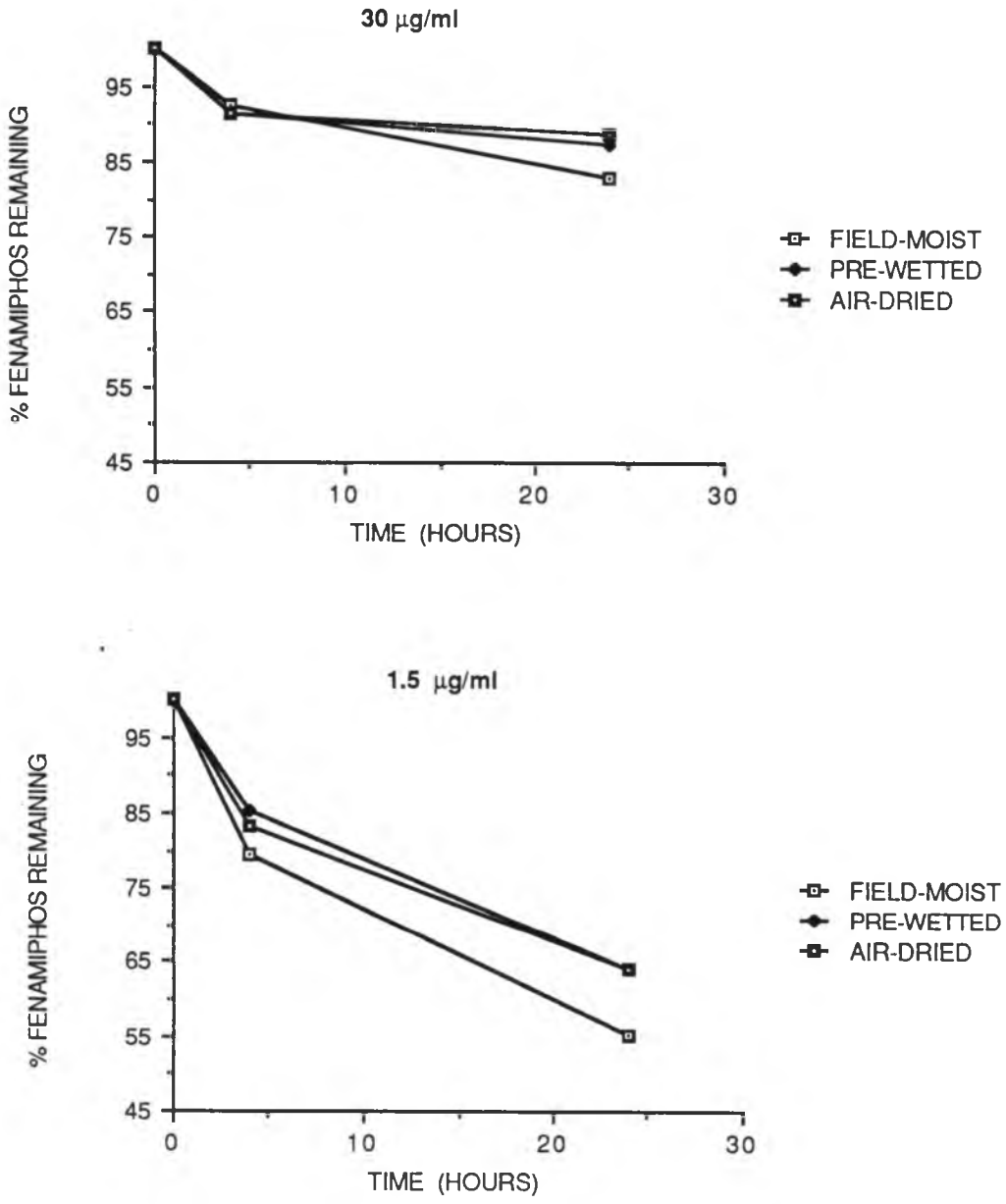

Figure 4 Effect of initial soil moisture content, concentration, and equilibration time on fenamiphos degradation during batch sorption measurements for Pane soil

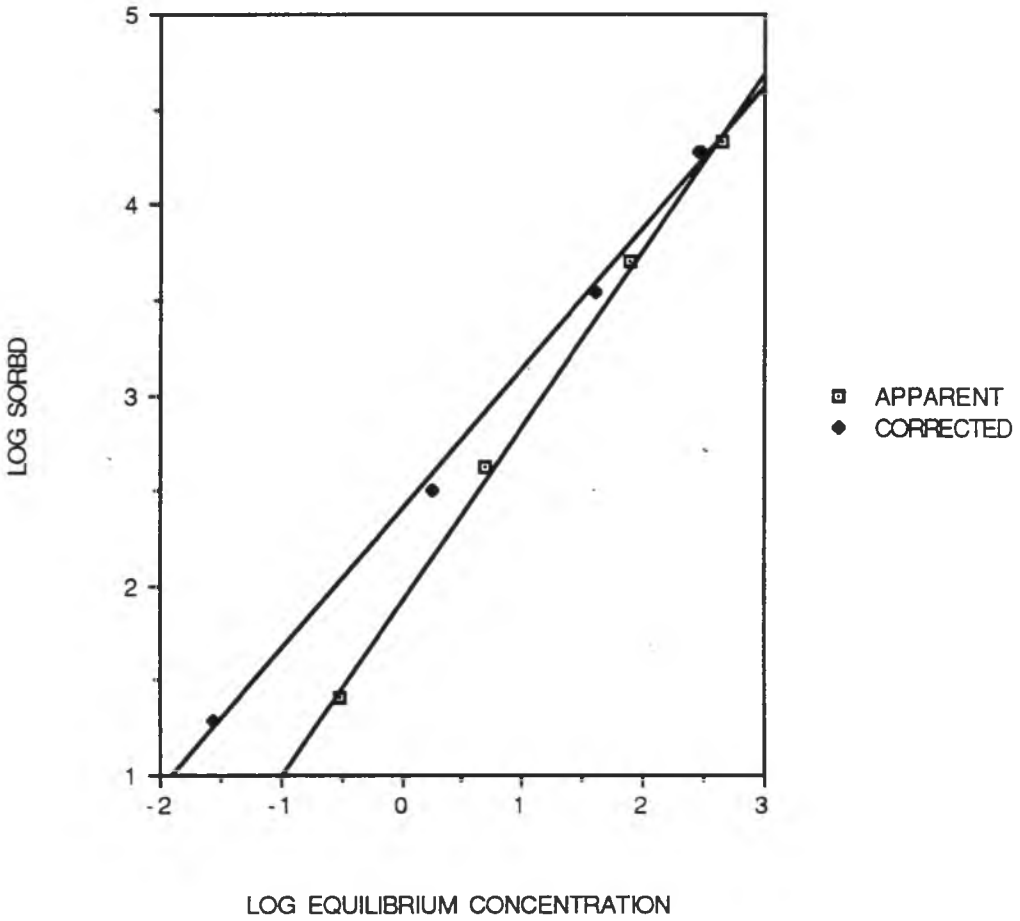

Figure 5 Effect of fenamiphos degradation at low intial concentration on isotherm slope (N) after 24 hours equilibration on air-dried Pane soil

in field-moist soils prior to sorption measurements. The greater microbial population would have an increased capacity to degrade fenamiphos. Therefore, both fenamiphos degradation and competitve effects of water for sorption sites may account for the lower apparent sorption recorded on field-moist soils. The latter effect of competition with water may still dominate because decreased sorption was measured even though the sorption data were corrected for fenamiphos degradation (table 1).

In prewetted soils, there was no evidence of an increase in degradation as compared with air-dried soils despite preincubation for 48 hours. In similar studies on diuron and aniline sorption on preincubated (48 hours preincubation) and air-dried soils, Dao et al.,(1982) concluded that no degradation occurred during the short (3 hours) equilibration time because no significant differences were found in the two moisture treatments. In our study with fenamiphos, it was expected that prewetted soils would behave similarly to field-moist soils, but the degradation evidence (discussed previously) and a higher sorption on prewetted than on field-moist soils showed that it was not true. This suggests that rewetting air-dried soil 48 hours prior to sorption measurement does not restore the soil to its original field-moist status. Complex changes in the physico-chemical properties such as stability and colloidal changes in organic matter (Raveh and Avnimelech, 1978,) and drastic fluctuations in microbial populations (Sparling and Cheshire, 1979; Stotsky et al., 1962) occur when soils are subjected to airdrying and rewetting procedures in the laboratory. Since the abovementioned properties directly affect sorption of labile organic chemicals, it is not surprising that prewetted soils would exhibit a different sorptive capacity than field-moist soils.

Molokai Soil

Fenamiphos was degraded at all moisture treatments by an average of 10% and 16% after 4 and 24 hours equilibration. Although there was evidence of fenamiphos degradation, apparent fenamiphos sorption increased with equilibration time by a factor of 1.3 for all moisture treatments (table 2). This is in contrast with a predicted decrease in apparent fenamiphos sorption . We suspect that true fenamiphos sorption equilibrium may not be attained even after 24 hours equilibration. The small amount of fen. sulfoxide formed from fenamiphos degradation may be masked by

the larger amount of fenamiphos remaining which may still be sorbing to the soil surface.

The apparent sorption coefficients after 4 and 24 hours equilibration did not change significantly after correction for fenamiphos degradation. Recall that similar results were obtained on corrected sorption data for Pane soil after 4 hours equilibration. The common feature of the foregoing experiments is that the error introduced from fenamiphos degradation on sorption measurements is negligble provided that the amount of fenamiphos degradation remains < 20%. The question of whether degradation was more rapid in moist rather than air-dried soils to effect an inflated sorption on air-dried samples cannot be elucidated in this soil because of the low amount of fenamiphos degradation.

Sorption variability

Although the effects of the three moisture treatments on fenamiphos sorption on the two soils were significantly different, the differences were not large. The percentage difference in fenamiphos sorption coefficients between air-dried and field-moist soils (D), expressed as $D = 100 \times (K_{fAD} - K_{fFM})/K_{fFM}$, after 24 hours equilibration were 34% and 37% for Pane and Molokai soil, respectively (tables 1 and 2). Variability of sorption data obtained from laboratory-generated batch experiments of surface soils obtained from nine large field areas typically showed CVs of 35% and 47% for fenamiphos and fen. sulfoxide, respectively (Green et al.,1985). A CV of 31% was found for napropamide sorption on soil samples obtained from a 0.6 ha field (Elabd and Jury, 1986); the authors considered the CV to be tolerable for modeling field behavior of this chemical. In an extensive study of spatial variability of sorption of two pesticides, metolachlor and aldicarb, on soils sampled from a 4.5 ha Georgia site, Rao et al. (1986) measured an average CV of about 50%. Considering the variability expected in the field, the errors by using sorption values obtained from air-dried soils may be tolerable for the purpose of modeling fenamiphos movement at the field scale. However, when one has the option of determining the preferred procedure for processing soil samples, it is appropriate to use field-moist samples.

CONCLUSIONS

Sorption of fenamiphos on both Pane and Molokai soils was higher (36%) on air-dried soil than field-moist soil; soils prewetted 48 hours before sorption measurements were generally intermediate in sorption. Degradation of fenamiphos to mainly fen. sulfoxide during batch equilibration occured at all moisture treatments and the impact of degradation (45% fenamiphos degraded) on sorption measurement was significant on the Pane soil. On Molokai soil, however, the impact was negligible because only less than 20% of fenamiphos degraded. Competition of water molecules with fenamiphos for sorption sites and fenamiphos degradation during equilibration were mainly responsible for the differences in sorption. The magnitude of the effect of initial soil moisture status on sorption measurements may not be important for practical field applications when we consider the normal spatial variability of sorption encountered in field soils.

CHAPTER III

DEGRADATION

RELIABILITY OF LABORATORY-MEASURED DEGRADATION OF NEMATICIDES FOR PREDICTION OF PERSISTENCE IN FIELD SOIL ENVIRONMENTS

INTRODUCTION

In recent years, several mathematical models have been developed with the purpose of predicting pesticide mobility and persistence in different soil environments from a large database of (a) climatic variables (rainfall, temperature), (b) management variables (irrigation, timing of pesticide application), and (c) pesticide and soil properties (sorption, degradation and soil hydraulic properties)(Wagenet and Rao, 1986; Nicholls et al., 1982; Walker and Barnes, 1981; Leistra et al., 1980). The accuracy and associated confidence in model output that represent field behavior are however, only as reliable as the accuracy with which the model input parameters can be measured either from laboratory (lab) or field experiments.

An important process, pesticide degradation, is commonly measured under lab conditions because the researcher can have complete control of the important factors (soil moisture content, temperature, pH, sorption and substrate concentration) that influence pesticide degradation. However, the reliability of utilizing lab-generated degradation data to predict field persistence has not been critically evaluated. The reliability is in question because spatial and temporal variations are operative under field situations to result in increased variability in pesticide residue concentrations. The contributors to variability in the field that often do not exist in lab environments include climate (fluctuating soil temperature and moisture regimes) and management factors (crop planted, irrigation, tillage and pesticide application mode).

Soil water content and temperature are considered the two most important environmental factors controlling pesticide degradation. Their influence on degradation has been thoroughly studied under lab conditions. Extensive work by Walker and co-workers (Walker, 1976a, 1976b, 1976c; Walker, 1978; Walker and Zimdahl, 1983; Walker et al., 1983) and Troester et al. (1984) have employed the Arrhenius (temperature-degradation relationship) equation coupled with power function equations (moisture-degradation dependence) to quantify the effects of

temperature and moisture on pesticide degradation under controlled lab environments. These parameter values and related meteorological data (soil temperature and moisture) were subsequently used as inputs in simple simulation models to predict the persistence of several pesticides in field microplots at numerous locations. The authors considered the model predictions to be acceptable for practical field applications in view of the possibility that other factors such as volatilization, leaching beyond the sampling zone, and photochemical degradation were not accounted for in the model but may be partly responsible for pesticide losses. However, in most of the cases investigated by Walker and co-workers, the model underestimated the residues remaining by a factor of two. After analyzing a large database of degradation data determined from lab and field methods on several pesticides, Rao and Davidson (1980) and Rao et al.(1983), concluded that for temperatures in the range of 15 to 35^{o}C and for soil moisture tensions (SMT) in the range of 0.1 to 1.0 bar, the half-life for a given pesticide does not vary significantly and thus can be estimated within a factor of two. The abovementioned studies imply that degradation data generated from the lab may under some conditions, predict field persistence with tolerable accuracy for field management purposes. The acceptability of the uncertainty is largely dependent on the intended use of the model predictions.

While changes in soil temperature and moisture can be evaluated in lab experiments, the management variable is rarely considered, probably because of the difficulty of conducting such experiments. Various field studies have demonstrated extreme variability in initial residue recoveries shortly after pesticide application. Taylor et al., (1971) detected a 50-fold difference in dieldrin residue with an associated coefficient of variation (CV) of 80%. Walker and Brown (1983) measured a CV of 60% in simazine residue recoveries. Both studies attributed the large variation to the uneveness in initial application from conventional boom sprayers. When application was performed carefully with a knapsack sprayer, Walker and Brown (1983) found a noticeable reduction in the variability of simazine recoveries (CV=17%). Similarly, Rao et al.(1986) demonstrated that two to three orders of magnitude differences in aldicarb total toxic residues (TTR) were measured in soil samples collected immediately after tillage and aldicarb application.

Additional differences between results from lab and field experiments are related to changes in soil biological, chemical and physical properties that occur from soil

preparation prior to conducting degradation experiments in the lab. Soil porosity which is directly related to the aeration status may change drastically after sieving and homogenizing field soils in the lab. Since microbial populations are extremely sensitive to environmental changes, lab manipulations such as air-drying, storage and re-wetting previously air-dried soils may reduce and/or alter microbial populations. Futhermore, because of the small amount of soil used in lab experiments, lack of sufficient substrate for microbial survival in long term incubations may pose another limitation in lab degradation studies.

The test compounds used in this study were two nematicides, fenamiphos and its major oxidation by-product, fenamiphos sulfoxide. These nematicides were selected because they have gained importance as a viable alternative to the recently banned fumigants (EDB and DBCP) for nematode control in pineapple fields. An earlier study (Lee et al., 1986) found that fenamiphos degraded very rapidly (half-life = 3 days) and was highly sorbed (K_f = 4.5 ml g^{-1}) on a Hawaiian Oxisol. Fen. sulfoxide in contrast, is more persistent (half-life= 80 days) and being more polar, is sorbed (K_f = 1.2 ml g^{-1}) less than fenamiphos. Little is known on the degradation of these compounds in different soil environments. Since it is impossible to measure degradation in all field situations, models will be used to assess field persistence and leaching potential of these nematicides from lab-generated degradation data and other soil-pesticide parameters. The model output will aid in developing optimum management strategies to achieve maximum efficacy and minimum environmental contamination.

The objective of this study is to evaluate the reliability of using lab-generated degradation rates to predict degradation under field conditions. The uncertainties in degradation measurements conducted in the lab are critically compared with (a) uncertainties associated with insitu degradation experiments at two field sites and (b) overall errors contributed from measurement of the degradation parameter.

MATERIALS AND METHODS

Field and Soil Description

Degradation experiments were performed in two fields at two different pineapple plantations, Dole and Del Monte. All fields had preplant fumigation treatment with Telone II (1,3-dicloropropene) and were mulched with black plastic to prevent volatilization losses. Fenamiphos was applied postplant with drip irrigation water in the Dole field whereas fenamiphos was applied through foliar application in the Del Monte field. The Del Monte field was unirrigated. The Dole crop was 5 years old and provided 100% canopy cover while the Del Monte crop was only one year old and provided 40% canopy cover. The Dole field occupies an area of 79 ha, relatively homogeneous and consisted of only one soil series. The soil type was a Lahaina silty clay and classified as clayey, kaolinitic, isohyperthermic, Typic Torrox. Soil properties such as organic carbon (ranging from 0.9-1.2%), pH (ranging from 5.0-5.8) were similar at all six locations. The Del Monte field is smaller in area (30 ha), more heterogeneous, and was selected to better test the objectives under variable field conditions. It had at least three soil series with the Kolekole and Kunia series being dominant in the selected locations; detailed soil properties are shown in table 3.

Field Experiments

In the design of field degradation experiments, we had to consider the controlled setup of laboratory degradation experiments where leaching does not account for nematicide loss. Also, we were only interested in characterizing degradation within the crop root zone. Preliminary field experiments were initiated using wide-mouth bottles (similar to experiments by Lavy, et al., 1973; see appendix B.1) containing soil treated with nematicides and later buried in the surface soil of the pineapple bed. Because of concerns regarding the lack of aeration and labor intensiveness in using the bottle technique for insitu degradation experiments, a modified method using open aluminum cylinders was designed.

Table 3 Selected Soil Properties of Del Monte Field

Location	OC[a]	pH[b]	Soil Water Content[c] 0.3 bar	1.0 bar	Major[d] Minerals	Soil Type[e]	Slope %
A	1.1	4.4	36.1	32.6	Kaolinite	KSC	0-3
B	0.9	4.5	36.4	33.4	Kaolinite	KSC	0-3
C	1.0	4.5	35.8	33.2	Kaolinite	KSC	0-3
D	1.7	4.7	45.3	30.5	FeO, G	KO	12-25
E	3.4	4.7	45.1	39.3	FeO, G	KO	1-6
F	5.0	4.5	60.6	53.0	FeO, G	KO	1-6

a % total carbon determined by dry combustion method
b determined in 1:1 soil:water
c % moisture by weight at specified moisture tension (bars)
d FeO, G (iron oxide and gibbsite)
e KSC (Kunia silty clay, fine, kaolinitic, isothermic, Ustoxic Humitropept), KO (Kolekole silty clay loam, fine, oxidic, isothermic, Ustoxic Humitropept)

Six locations consisting of pineapple beds (50 m length by 1 m width) were selected from both the Dole and Del Monte fields. Distances between locations were about 350 m and 150 m at Dole and Del Monte fields, respectively. Ten aluminum cylinders (7.2 cm diameter by 12.7 cm long) were installed at each location (fig. 6). The aluminum cylinders were separated by about 40 cm and placed in the middle of the bed (beside the drip irrigation line at the Dole field). Each cylinder was carefully inserted into the surface soil until 2 cm remained above the soil surface. After placement of cylinders, each of the cylinders was marked randomly with a specific sampling time at each location. Sampling times were 0, 3, 7, 14, and 21 days for fenamiphos degradation experiments and 0, 14, 28, 42 and 56 days for fen. sulfoxide. At specified sampling times, two replicate cylinders were excavated from each field location and immediately placed in ice-coolers and brought to the laboratory for processing on the same day. Fenamiphos experiments were conducted on the Dole field in April, 1986 and the Del Monte field in May, 1986. Fen. sulfoxide experiments were only performed on the Del Monte field from July to August, 1986.

The appropriate volume of nematicide solution required, such that the nematicide did not leach out of the soil column contained in the aluminum cylinder, was determined by preliminary experiments in the lab (Appendix B.2). The nematicide materials used were commercial emulsifiable formulation of fenamiphos (15% a.i.) and an experimental formulation of fen. sulfoxide (15% a.i.). Dosage in the field was accomplished as follows: About 1 cm of soil was removed from the top of each core, then 25 ml of an aqueous solution of fenamiphos (36 μg/ml) or 10 ml of fen. sulfoxide (180 μg/ml) were slowly applied to the exposed surface of each core with a 25 ml delivery pipette. After dosage, the previously removed soil was then replaced on the treated surface and the top of the cylinders were covered with a small piece of aluminum foil to prevent rainfall penetration. Assuming that the nematicides were evenly distributed in the top 3 cm soil depth (Appendix B.2), the final concentration in the soil was about 7 μg fenamiphos/ g soil or 13 μg fen. sulfoxide/ g soil. However, non-uniform distribution is likely to occur and the effect of different concentrations of fenamiphos and fen. sulfoxide on degradation rates was addressed in appendix B.4. The final concentration of fenamiphos approximates the actual rate of

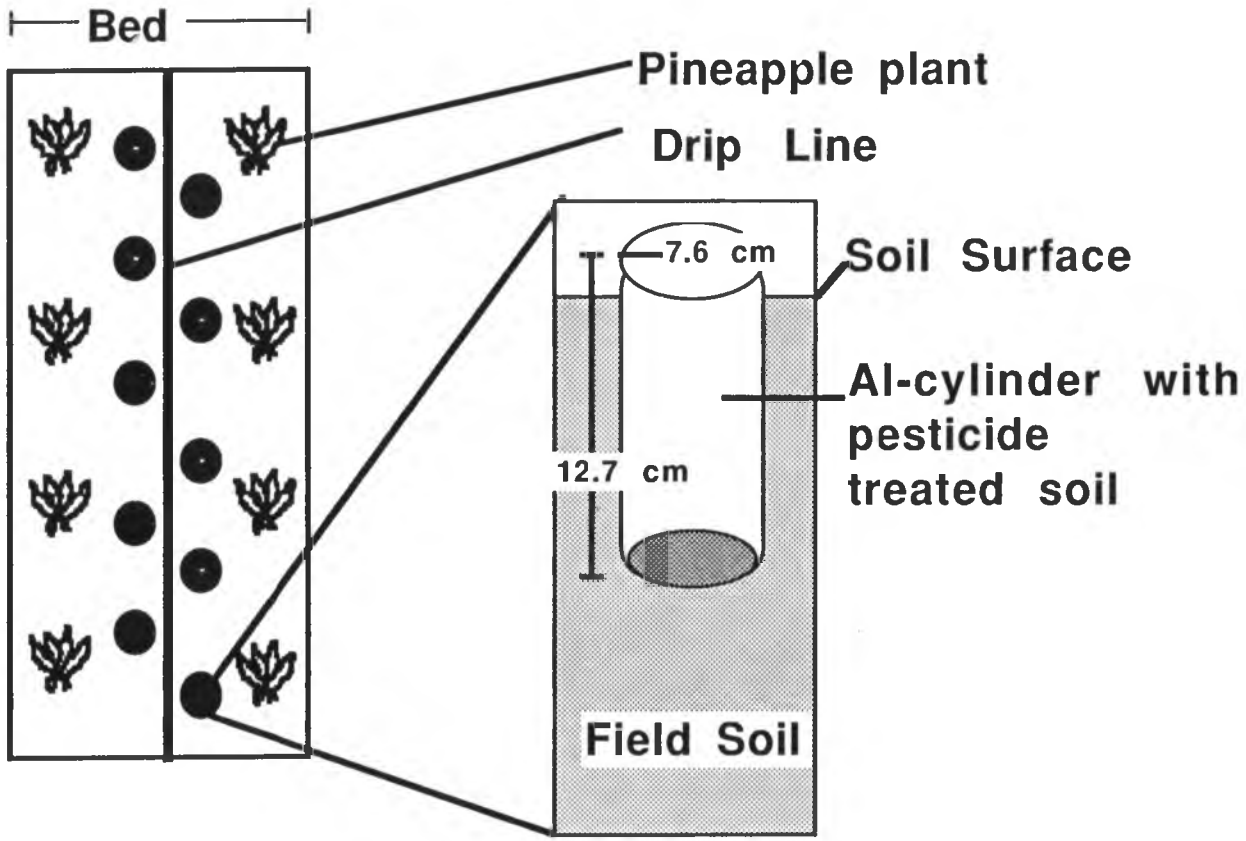

Figure 6 Schematic of field degradation experiment

application in pineapple fields. Fen. sulfoxide concentration however, was dosed much higher than residues expected to be found in the field situation because the detection limits of fen. sulfoxide by gas chromatography was five times lower than fenamiphos.

Soil temperature was monitored every two to three days in each location with two instantaneous soil temperature probes placed in the surface 0-9 cm depth. At two selected locations per field, two maximum/minimum thermometers were placed near the temperature probes (Appendix B.3). Soil moisture fluctuations were small and were readily recorded by soil moisture analysis of soils in the cores after sampling.

Laboratory Experiments

Surface soil samples (0-15 cm) collected from each location of the field experiments were passed through a 2 mm sieve and used in lab degradation studies as soon as possible after sampling. Lab experiments were performed within two weeks after initiation of field experiments. Moist soils equivalent to 16 g oven-dried weight were put on aluminum foil and dosed individually with one ml of an aqueous dilution of radiolabeled nematicide to achieve a final concentration of 8 µg fenamiphos/ g soil or 15 µg fen. sulfoxide/ g soil. Both fenamiphos and fen. sulfoxide were ring-14-C labeled, specific activity of 7.86 mCi/mM and > 95% pure. Aqueous dilutions of radiolabeled nematicide were made by mixing 14C- fenamiphos with an appropriate aliquot of emulsifiable grade fenamiphos to yield a 14C:12C ratio of 1:20; fen. sulfoxide radiolabeled solutions were prepared similarly with an experimental formulation of fen. sulfoxide. Additional water, if necessary, was added to adjust the soil to the appropriate soil water content. After mixing, the treated soils were transferred to culture tubes (2 cm x 15 cm) and capped tightly with a permeable membrane cap (Kimble). The permeable cap permitted free exchange of oxygen and CO_2 while maintaining minimal moisture loss. Radiolabeled fenamiphos and fen. sulfoxide were used in laboratory experiments because of time-savings, ease of use and analytical accuracy; minimum sample cleanup is required and liquid scintillation detection is extremely stable. Furthermore, preliminary studies (appendix B.1) have demonstrated that there was no significant difference between degradation half-lives of fenamiphos determined in the laboratory using radiolabeled fenamiphos as compared with using emulsifiable fenamiphos. Soils selected from two locations (A and C from Dole field and, A and F from Del Monte field) were incubated at a range of

soil moisture tensions from 0.3 to 1.0 bar (30 to 100 kPa) and three soil temperatures (15, 23 and 35^{o}C). The narrow range of SMT was selected because surface soils in irrigated pineapple fields rarely dry to > 1.0 bar moisture tension (Appendix B.3). The soil samples collected from the other locations were incubated at 23^{o}C and 1.0 bar moisture tension. Sampling times for nematicide analyses were similar to the field setup.

Extraction and Analyses

After the aluminum cylinders were removed from the field and brought to the lab, soil from the 0 to 8 cm depth of the cylinder was removed (about 300-400 g) and thoroughly mixed by hand in an aluminum pan. Duplicate subsamples (40 g) were taken into cellulose thimbles and extracted in a Soxhlet apparatus with 400 ml nanograde acetone for four hours. Subsamples were also taken for moisture analyses. After extraction, acetone extracts were rotoevaporated under vacuum at 40^{o}C until near dryness. For cleanup of water-soluble organics extracted from the soil, 25 ml of benzene were added to the residue and further rotated on the roto-evaporater for 10 min to facilitate partitioning of fenamiphos and metabolites into the benzene layer. After addition of Na_2SO_4 to remove water, the residue was filtered through glass filter paper. The clear brownish filtrate was transferred to a 15 ml graduated centrifuge tube and subjected to further cleanup using silica Sep-Pak cartridges (Millipore). After cleanup, the samples were ready for gas chromatographic (GC) analyses.

A Hewlett-Packard (HP) 5890A GC with a nitrogen-phosphorus detector (NPD) and an HP 3392A Integrator were used. A DB-5 (J & W Scientific) bonded fused silica capillary column (15 m X 0.25 mm ID, 25 µm film thickness) was used with a split-splitless injector in the split mode of 1:20 split ratio. Helium was employed as the carrier gas with an average linear velocity of 49 cm/s and a column head pressure of 14 psi. NPD combusion gas setings for hydrogen and air were 4.0 and 80 ml/min, respectively. A nitrogen makeup carrier of 33 ml/min was also used. The NPD bead was set at 20 pA (± 3 pA). Optimum temperatures for injector, oven and detector were 280^{o}C, 200^{o}C and 275^{o}C, respectively. Retention times were 5.5, 10.7 and 11.2 min for fenamiphos, fen. sulfoxide and fenamiphos sulfone, respectively. For fenamiphos and fen. sulfoxide experiments, only the applied

compound was quantified using peak area and an external standard method.

For the companion lab experiments utilizing radiolabeled nematicides, the entire soil content was removed from replicate culture tubes for soxhlet extraction. Subsequently, the extraction procedure was similar to that of the field sample up to the benzene cleanup step. Aliquots of the benzene extract were subjected to thin-layer chromatography and the fraction of radioactivity remaining as fenamiphos and metabolites was quantified by liquid scintillation methods according to Cheng-Tseu et al., 1987.

Blank soils were also extracted from both Dole and Del Monte fields Since background levels of fenamiphos and fen. sulfoxide were found at the detection limit, no correction was made on the degradation data. Zero-time recoveries of nematicides (fenamiphos and fen. sulfoxide) from radiolabeled and field samples were >85% and >75%, respectively. The recovery was probably lower in field core samples because of losses from mixing and subsampling from bulk soils. These recoveries were assumed to apply for extractions accomplished at all sampling times, and measured concentrations were adjusted accordingly.

Data Analyses

The degradation data were fitted by the first-order kinetic equation,

$$\text{Ln } C/C_0 = -kt \qquad [2]$$

where C is the concentration of nematicide remaining in the acetone extractable portion at time t, C_0 is the initial concentration at time 0, and k is the first-order degradation rate coefficient. The intercepts were tested for difference from 0 in order to evaluate deviations from first-order kinetics. First-order half-lives ($t_{0.5}$) were computed from the relationship,

$$t_{0.5} = \text{Ln } (0.5)/k \qquad [3]$$

Confidence intervals (95%) of the degradation rate coefficients and half-lives were calculated from the standard errors (SE) of k and $t_{0.5}$ respectively with the appropriate student's t-value. The SE of $t_{0.5}$ ($SE_{t0.5}$) is related to the SE of k (SE_k)

by the expression,

$$SE_{t0.5} = (0.693/k^2) \times SE_k \qquad [4]$$

This relationship is obtained with the expression derived by Kempthorne and Allmaras (1965) for the variance of a derived function, where the variance of x is s_x^2 and the variance of f(x) is

$$\{\partial/\partial x\,[f(x)]\}^2\ s_x^2 \qquad [5]$$

When [5] is applied to equation [3] and knowing that $SE^2 = s^2/n$, where n = number of samples, the result is equation [4].

Calculation of confidence intervals on this basis will lead to upper and lower limits that are equidistant from the mean estimated half-lives. Erroneous (skewed) confidence intervals will result if the confidence intervals of the half-lives are calculated by merely dividing the term Ln(0.5) by the upper and lower limits of k. The result is especially pronounced for very persistent compounds ($k < 0.01$ day^{-1}). An example of this skewed confidence interval calculated by the above method was found in data reported by Lightfoot et al. (1987) from lab experiments conducted on degradation of aldicarb TTR (see table 4). Recalculation of the confidence intervals based on equation (4) yielded much lower values of the upper and lower limits, but the difference between the estimated $t_{0.5}$ and the upper and lower half-lives was the same (1344 days).

Temperature dependence of degradation was quantified by fitting k at respective temperatures to the Arrhenius equation,

$$\text{Ln } k = -(Ea/R)/T + \text{Ln } B \qquad [6]$$

where Ea is the activation energy (kJ mol^{-1}), R is the gas constant (8.31 J K^{-1}mol^{-1}), T is the absolute soil temperature (degree Kelvin), and B is the frequency factor constant (day^{-1}). Since fenamiphos degradation rates from A and C Dole field locations were similar, k values were pooled from both locations and fitted to the Arrhenius equation. Fenamiphos and fen. sulfoxide degradation data from A and F locations at Dole Monte field locations were fitted separately.

Table 4 Recalculation of Confidence Intervals of Degradation Half-lives of Aldicarb Total Toxic Residues from Lightfoot et al. (1987)

	Estimated $t_{0.5}$	SE	95% confidence interval		Difference from Estimated $t_{0.5}$	
			upper	lower	upper	lower
k*	3.6	1.17	6.12	1.09	-	-
$t_{0.5}$†	1924	-	6370	1133	4446	791
$t_{0.5}$§	1924	627	3268	580	1344	1344

† first-order degradation half-lives (day) and associated 95% confidence interval extracted from table 1, Lightfoot et al. (1987)

* first-order degradation rate (x 10^{-4} day^{-1}) calculated from equation [3] and standard error (SE) was calculated assuming 14 observations and student t = 2.145

§ first-order degradation half-lives (day); SE was calculated from equation [4]

RESULTS AND DISCUSSION

Fit to First-Order Kinetics

Pesticide degradation data are commonly reported to fit first-order kinetics but deviations from first-order are known to occur (Hance and Haynes, 1981). The first-order kinetic equation is frequently employed because it is a simple equation to use for modeling pesticide persistence and it often fits experimental data well. Furthermore, no one rate equation is likely to be completely adequate for any single pesticide over its entire period of degradation (Goring et al., 1975). It is disturbing to find that in the majority of research papers dealing with pesticide degradation, the only criteria used for judging goodness of fit of first-order kinetics is a significance test to the fit (at a certain probability level) and the associated coefficient of determination, r^2. If the form of the first-order kinetics model is expressed as equation (2), and a regression analysis of Ln C/Co against t is performed, r^2 cannot be calculated (see example of regression through the origin in Steel and Torrie, 1983). If an intercept (b) is included in the model i.e.,

$$\text{Ln } (C/C_o) = -kt + b \qquad [7]$$

r^2 can be computed but the question of whether the intercept is zero must be statistically tested. If the intercept is significantly different from zero, then the first-order kinetics model is clearly violated. Alternatively, the intercept can be tested for significant difference from Ln C_o if the expression of the first-order kinetics model is in the form of

$$\text{Ln } C = -kt + \text{Ln } C_o \qquad [8]$$

Neither of the intercept tests for violations from first-order kinetics in equations [7] and [8] are reported in the degradation literature.

We chose to use the former approach to fit the degradation data of fenamiphos and fen. sulfoxide to equation [7] with an intercept. The estimated rate coefficients, half-lives and their associated 95% confidence interval, and the r^2 and intercept values are presented in tables 5 to 7. With the exception of two locations (where $r^2 < 0.55$), r^2 values were generally better than 0.70, indicating that the first-order kinetics equation fit the data with a significance level of $P < 0.05$. Note

Table 5 Laboratory and Field Degradation First-order Rate Coefficients and Apparent Half-Lives of fenamiphos for Dole Field.

LOCATION	METHOD	k ($x10^{-2}$ day^{-1})	$t_{0.5}$ (day)	b ($x\text{-}10^{-2}$)	r^2
A†	LAB††	9.37 (6.17-12.6§)	7.4 (4.9-9.9)	56.6 *	0.880
	FIELD	6.15 (4.07-8.22)	11.2 (7.5-15.0)	32.8 *	0.876
B	LAB	8.26 (4.55-12.0)	8.4 (4.6-12.1)	47.1 *	0.832
	FIELD	9.57 (5.33-13.8)	7.2 (4.0-10.4)	16.9 ns	0.803
C	LAB	10.1 (7.07-13.0)	6.9 (4.9-8.9)	37.4 *	0.919
	FIELD	7.13 (3.67-10.6)	9.7 (5.0-14.4)	35.1 ns	0.773
D	LAB	7.64 (3.52-11.8)	9.1 (4.2-13.9)	37.4 *	0.775
	FIELD	6.54 (6.17-6.90)	10.5 (10-11.1)	41.7 *	0.847
E	LAB	8.80 (6.35-11.3)	7.9 (5.7-10.0)	55.6 *	0.917
	FIELD	9.44 (7.68-11.2)	7.3 (6.0-8.7)	12.8 ns	0.958
F	LAB	7.26 (4.87-9.64)	9.5 (6.4-12.6)	39.3 *	0.903
	FIELD	7.69 (6.83-8.55)	9.0 (8.0-10.0)	9.6 ns	0.812
OVERALL	LAB	8.58 (7.49-9.66)	8.1 (7.1-9.1)	45.8 *	0.841
	FIELD	7.76 (6.70-8.82)	8.9 (7.7-10.2)	24.8 *	0.805
CV (%)	LAB	12.2			
	FIELD	17.9			

† t-test was used to compare k-values generated by laboratory and field method at each location; comparisons at all locations were not significantly differrent.

†† laboratory degradation rate determined at 23^0C and 0.3 bar moisture tension.

§ numbers in parenthesis are the 95% confidence interval

ns, * nonsignificant and significant difference at 0.05 level, respectively. F-test was used to test if the intercepts were significantly different from 0.

Table 6 Laboratory and Field Degradation First-order Rate Coefficients and Apparent Half-Lives of fenamiphos for Del Monte Field.

LOCATION	METHOD	k ($x10^{-2}$ day^{-1})	$t_{0.5}$ (day)	b ($x\text{-}10^{-2}$)	r^2
A†	LAB††	14.0 (12.9-15.1§)	5.0 (4.6-5.3)	6.4 ns	0.996
	FIELD	10.4 (7.9-12.9)	6.7 (5.1-8.2)	7.2 ns	0.934
B	LAB	14.7 (12.6-16.8)	4.7 (4.1-5.4)	18.3 ns	0.982
	FIELD	11.9 (9.4-14.4)	5.8 (4.6-7.1)	17.7 ns	0.947
C	LAB	15.4 (12.6-18.2)	4.5 (3.7-5.3)	23.7 ns	0.971
	FIELD	12.5 (9.2-15.8)	5.5 (4.1-7.0)	0.4 ns	0.920
D	LAB	5.35 (2.54-8.16)	12.9 (6.2-19.7)	21.5 ns	0.802
	FIELD	5.17 (0.24-10.1)	13.4 (0.63-26.2)	64.9 *	0.468
E	LAB	7.36 (5.40-9.32)	9.4 (6.9-11.9)	11.7 ns	0.940
	FIELD	8.12 (3.20-13.0)	8.5 (3.4-13.7)	2.3 ns	0.686
F	LAB	5.24 (4.41-6.05)	13.2 (11.2-15.3)	3.5 ns	0.980
	FIELD	3.43 (1.59-5.26)	20.2 (9.4-31.1)	4.2 ns	0.736
OVERALL	LAB	10.36 (7.68-13.0)	6.7 (5.0-8.4)	14.1 ns	0.610
	FIELD	8.59 (6.69-10.5)	8.1 (6.3-9.9)	16.0 ns	0.613
CV (%)	LAB	49.7			
	FIELD	57.7			

† t-test was used to compare k-values generated by laboratory and field method at each location; comparisons at all locations were not significantly different.

†† laboratory degradation rate determined at 23^0C and 1.0 bar moisture tension.

§ numbers in parenthesis are the 95% confidence interval

ns, * nonsignificant and significant difference at 0.05 level, respectively. F-test was used to test if the intercepts were significantly different from 0.

Table 7 Laboratory and Field Degradation First-order Rate Coefficients and Apparent Half-Lives of fen. sulfoxide for Del Monte Field.

LOCATION	METHOD	k ($x10^{-2}$ day^{-1})	$t_{0.5}$ (day)	b ($x-10^{-2}$)	r^2
A†	LAB††	1.52 (1.11-1.93§)	45.5 (33.3-57.9)	7.6 ns	0.943
	FIELD	1.33 (0.88-1.78)	51.9 (34.4-69.6)	12.9 ns	0.875
B	LAB	1.41 (0.81-2.00)	49.1 (28.3-70.1)	3.8 ns	0.869
	FIELD	0.91 (0.43-1.38)	76.1 (36.5-115.8)	7.9 ns	0.746
C	LAB	1.31 (0.81-1.80)	52.9 (32.9-73.1)	2.9 ns	0.710
	FIELD	1.23 (0.59-1.86)	56.2 (27.3-85.2)	14.3 ns	0.751
D	LAB	1.04 (0.39-1.69)	66.3 (25.1-107.4)	17.8 ns	0.756
	FIELD	1.40 (1.03-1.75)	49.6 (36.7-62.6)	15.0 ns	0.922
E	LAB	1.16 (0.66-1.64)	59.9 (34.7-85.1)	14.9 ns	0.871
	FIELD	1.63 (1.03-2.21)	42.6 (27.2-58.1)	3.3 ns	0.859
F	LAB	1.06 (0.52-1.58)	65.6 (32.8-98.6)	8.7 ns	0.826
	FIELD	1.02 (0.16-1.87)	68.1 (10.8-125.4)	16.7 ns	0.530
OVERALL	LAB	1.25 (1.07-1.43)	55.4 (47.5-63.5)	9.3 ns	0.830
	FIELD	1.25 (1.03-1.47)	55.3 (45.5-65.2)	11.6 ns	0.711
CV (%)	LAB	15.4			
	FIELD	21.8			

† t-test was used to compare k-values generated by laboratory and field method at each location; comparisons at all locations were not significantly differrent.

†† laboratory degradation rate determined at 23^0C and 1.0 bar moisture tension.

§ numbers in parenthesis are the 95% confidence interval

ns, * nonsignificant and significant difference at 0.05 level, respectively. F-test was used to test if the intercepts were significantly different from 0.

however the large variations in the calculated 95% confidence interval of the half-lives, ranging from 25 to 107 days (factor of 4) for fen. sulfoxide (table 7, location D) and from 9.4 to 31 days (factor of 3) for fenamiphos (table 6, location F), even though r^2 values were >0.75 for these locations. Standard errors of first-order degradation rates and related confidence limits are not reported in most degradation studies. Those that document these error estimates showed that the standard error of the first-order degradation rates contributed maximum deviations of 12% (Hance and Haynes, 1981) and 20% (Walker and Smith, 1979) from the mean degradation rates. Confidence intervals of degradation half-lives reported by Lightfoot et al.(1987) for lab degradation studies on aldicarb and toxic metabolites (aldicarb sulfoxide and sulfone) exhibited large differences (factor of 2 to 4), similar to those found in this study. Since there are always uncertainties in degradation measurements, it is thus imperative to include error estimates of the calculated half-lives such that the confidence in or reliability of the half-lives can be readily evaluated. This point is particularly useful for modelers who need confidence limits associated with the degradation parameter rather than absolute values in order to assess the impact of a range of degradation rates on modeling persistence in the field environment.

Tests of intercepts for deviations from zero (i.e. deviations from first-order kinetics) revealed that the violations occurred mainly in the degradation of fenamiphos in the Dole-field lab experiments (table 5); all lab data for this field had significant intercepts. This apparent uniqueness of the Dole-field lab data, however, must be interpreted in the context of overall variability. Statistically significant differences are more likely to occur when the error variance is small. Hence, the Dole-field fenamiphos lab data, which has the lowest overall CV (12,2%, table 5) showed a significant intercept in all cases, while the Del Monte-field fenamiphos lab data (table 6) have a much higher CV (49.7%) and no significant intercepts. The much higher overall variability of the Del Monte field relative to the Dole field is evident also in a comparison of first-order degradation plots in figures 7 and 8. It is difficult, therefore, to know what probability level is appropriate to denote significant differences when general variance levels are greatly different between experiments. Thus, even though the degradation kinetics appear to deviate from first-order in some cases, the error in assuming first-order kinetics may be

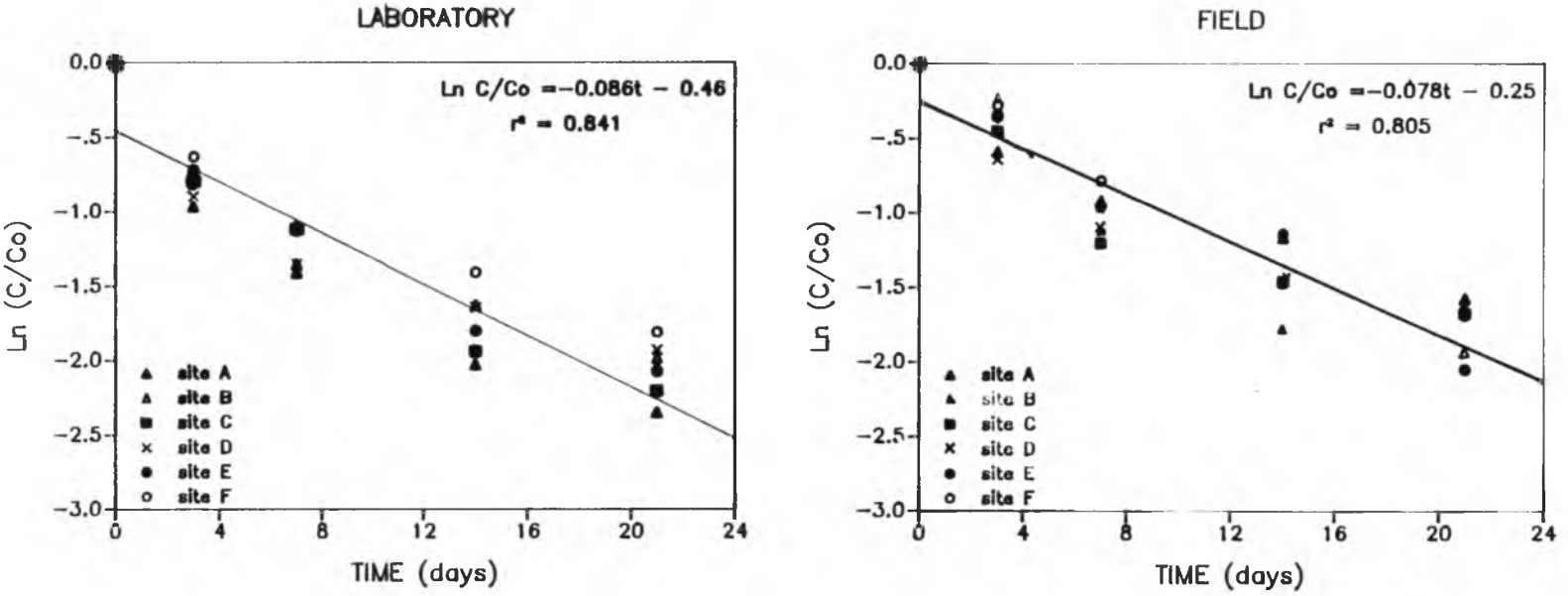

Figure 7 Laboratory and field degradation of fenamiphos for Dole field

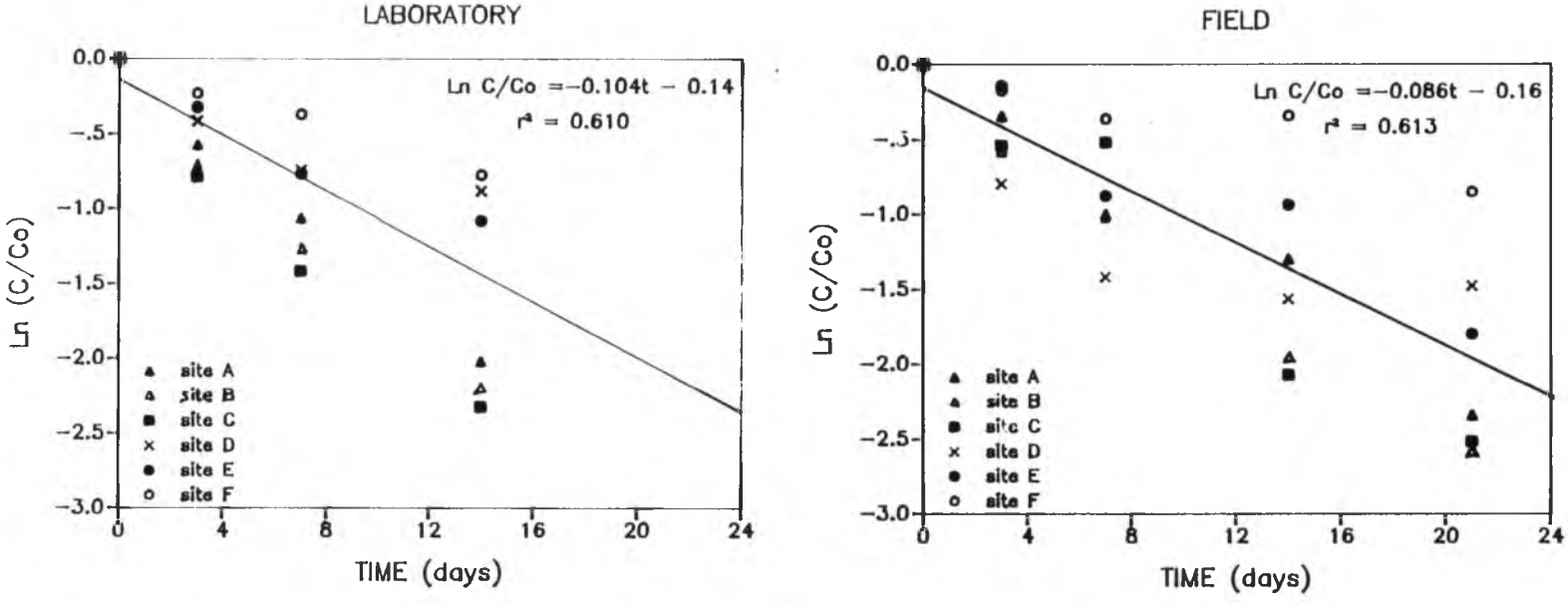

Figure 8 Laboratory and field degradation of fenamiphos for Del Monte field

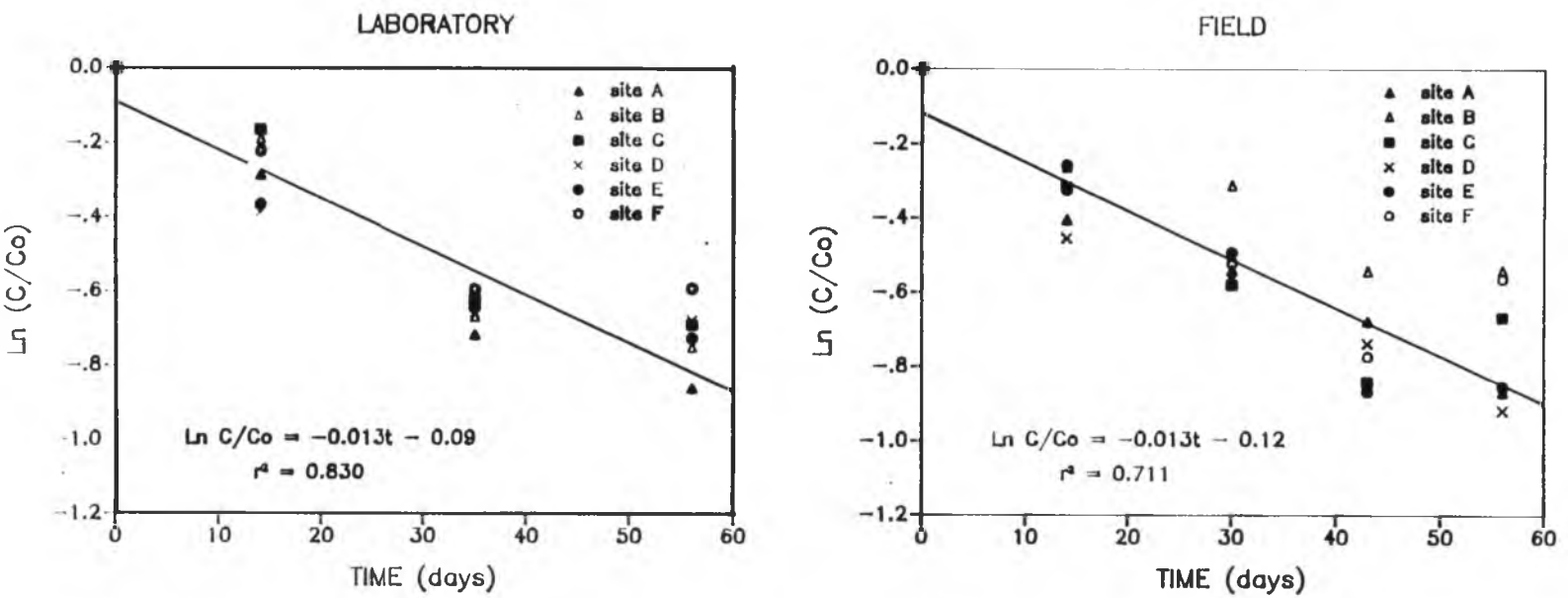

Figure 9 Laboratory and field degradation of fenamiphos sulfoxide for Del Monte field

acceptable if we consider other sources of error from field variability and analytical techniques. These errors will be discussed in more detail in later sections.

Effect of Moisture on Degradation

Temperature and moisture dependence of fenamiphos and fen. sulfoxide degradation at two selected locations from Dole and Del Monte fields are shown in tables 8 to 10. Moisture treatments were not performed on samples from Dole field because preliminary studies on a similar Oxisol (Appendix B.1) have shown that there was no significant effect of moisture (0.1 to 1.0 bar) on fenamiphos degradation. Note that fenamiphos and fen. sulfoxide degradation on soils from Del Monte field exhibited a trend of increasing degradation at lower soil moisture tension; the difference however, was not significant. At such a narrow range of SMT, experiments by Ou et al. (1983) have demonstrated that the effects on the half-lives of two pesticides were essentially constant. In the range of 0.1 to 0.33 bar soil-moisture tension, the mineralization rates of 2,4-D in four soils were not affected. Similarly, degradation rates of propachlor were identical even though the soil-moisture tension ranged from 0.1 to 1.0 bar. In more recent work by Ou and Rao (1986) however, the half-lives of fenamiphos total toxic residues (i.e. fenamiphos, fen. sulfoxide and fen. sulfone) decreased by a factor of two associated with a reduction in soil-moisture tension from 1.0 to 0.1 bar.

Under the field conditions of irrigated pineapple, the expected range of SMT is only from 0.1 to 1.0 bar. In fact, for the unirrigated Del Monte field, SMT of soils in the aluminum cylinders rapidly redistributed to a tension of 1.0 bar three days after nematicide application and remained at this tension for the rest of the experiment (Appendix B.3). Moisture content was higher for the irrigated Dole field, and the average SMT was about 0.3 bar. Hence, for the purpose of comparing lab and field degradation rates, we can justify using degradation data determined from a single appropriate moisture tension in the lab without having to account for fluctuating moisture conditions in the field. It is important to note that in cases where there is a substantial effect of SMT on degradation, the dependence of half-life on moisture can be described by a power function equation,

Table 8 Effect of Temperature on Fenamiphos Degradation in Soil from Two locations of the Dole Field.

Temp (^{0}C)	Moisture Tension (bar)	Locations			
		A		C	
		k ($X10^{-2}$ day^{-1})	$t_{0.5}$ (day)	k ($X10^{-2}$ day^{-1})	$t_{0.5}$ (day)
15	0.3	5.08 (3.42-6.73†)	13.6 (9.1-18.3)	4.69 (4.19-5.19)	14.7 (13.2-16.4)
23	0.3	9.37 (6.17-12.6)	7.4 (4.9-9.9)	10.1 (7.07-13.0)	6.9 (4.9-8.9)
35	0.3	31.6 (18.7-44.5)	2.2 (1.3-3.1)	27.5 (12.2-42.8)	2.5 (1.1-3.9)
Ln B			15.7 [4.1 §]		
Ea ($x10^3$ kJ/mol)			-68.8 [2.6]		
r^2			0.994		
Predicted¶					
19 C		4.32	16.1 (14.1-18.2)		
24 C		6.96	10.0 (9.1-10.9)		

† numbers in parentheses are the 95% confidence intervals
§ numbers in brackets are the standard errors
¶ predicted half-lives and associated 95% confidence interval for range of field measured temperature from best-fit Arrhenius equation

Table 9 Effect of Temperature on Fenamiphos Degradation in Soil from Two Locations of the Del Monte Field.

Temp (°C)	Moisture Tension (Bars)	Locations			
		A		F	
		k ($X10^{-2}$ day^{-1})	$t_{0.5}$ (day)	k ($X10^{-2}$ day^{-1})	$t_{0.5}$ (day)
15	0.3	7.00 (4.81-9.19†)	9.9 (6.8-13.0†)	2.95 (2.10-3.79)	23.4 (16.7-30.2)
	1.0	6.20 (5.11-7.28)	11.1 (9.2-13.1)	2.56 (2.07-3.04)	27.0 (21.9-32.2)
23	0.3	15.4 (13.1-17.7)	4.5 (3.8-5.2)	6.23 (4.91-7.54)	11.1 (8.8-13.5)
	1.0	14.0 (12.9-15.1)	5.0 (4.6-5.3)	5.24 (4.41-6.05)	13.2 (11.2-15.3)
35	0.3	16.4 (7.99-24.8)	4.2 (2.1-6.4)	11.81 (9.68-13.9)	5.9 (4.8-6.9)
	1.0	18.4 (12.4-24.4)	3.8 (2.5-5.0)	8.55 (7.54-9.55)	8.1 (7.2-9.1)
Ln B			11.9 [3.6§]		16.4 [2.7]
Ea ($x10^3$kJ/mol)			-35.2 [9.1]		-48.5 [6.8]
r^2			0.789		0.928
Predicted¶					
20 C		9.78	7.1 (5.2-9.6)	4.14	16.8 (13.3-21.1)
28 C		14.18	4.9 (3.6-6.6)	6.90	10.0 (8.0-12.6)

† numbers in parentheses are the 95% confidence intervals
§ numbers in brackets are the standard errors
¶ predicted half-lives and associated 95% confidence interval for range of field measured temperature from best-fit Arrhenius equation

Table 10 Effect of Temperature and Moisture on Fen. sulfoxide Degradation in Soil from Two Locations of Del Monte Field.

Temp (^{0}C)	Moisture Tension (bar)	Locations			
		A		F	
		k ($X10^{-2}$ day^{-1})	$t_{0.5}$ (day)	k ($X10^{-2}$ day^{-1})	$t_{0.5}$ (day)
15	0.3	1.62 (0.51-2.71†)	42.8 (13.7-72.0)	1.14 (0.42-1.85)	60.7 (22.6-98.8)
	1.0	1.47 (0.30-2.63)	47.1 (9.7-84.6)	1.06 (0.52-1.58)	65.6 (32.8-98.6)
23	0.3	2.07 (1.79-2.34)	33.4 (29.0-38.0)	2.35 (1.63-3.07)	29.4 (20.4-38.5)
	1.0	1.52 (1.11-1.93)	45.5 (33.3-57.9)	1.45 (0.32-2.56)	47.9 (10.7-85.2)
35	0.3	3.06 (1.37-4.73)	22.6(10.2-35.1)	2.51 (0.88-4.12)	27.6 (9.8-45.5)
	1.0	2.20 (0.45-3.93)	31.5 (6.6-56.5)	2.41 (0.87-3.94)	28.7 (10.5-47.1)
Ln B			4.1 [2.6 §]		7.8 [3.1]
Ea ($x10^3$ kJ/mol)			-20.1 [6.4]		-29.9 [7.8]
r^2			0.712		0.787
Predicted¶					
22 C		1.82	38.1 (31.3-46.5)	1.56	44.3 (34.8-56.4)
30 C		2.22	30.9 (24.5-39.1)	2.14	32.5 (24.5-43.1)

† numbers in parentheses are the 95% confidence intervals
§ numbers in brackets are the standard errors
¶ predicted half-lives and associated 95% confidence interval for range of field measured temperature from best-fit Arrhenius equation

$$t_{0.5} = AM^{-B} \qquad [9]$$

(where M is the soil moisture content and A and B are constants) as proposed by Walker (1974). This model can then be used to extrapolate lab data to field conditions for prediction of degradation at any field measured soil moisture content.

Effect of Temperature on Degradation

Temperature variation is known to have a greater effect on degradation than moisture. Fenamiphos and fen. sulfoxide degradation were strongly influenced by temperature. An increase in temperature from 15 to 35°C resulted in a decrease in the half-life of fenamiphos by factors of 3 and 6 on soils from Del Monte and Dole fields, respectively (tables 8 and 9). For fen. sulfoxide however, the half-life was decreased only by a factor of 2 for the same increase in temperature (table 10). These values are comparable to those reported by Walker et al. (1983), who found that a change in temperature from 10 to 30°C increased the degradation rate of simazine by a factor of 2 to 5 on 21 soils collected from various countries. Ou et al. (1983) demonstrated that propachlor half-lives decreased by a factor of 2 when the temperature increased from 15 to 25°C. This decrease was consistent for three SMT levels ranging from 0.1 to 0.33 bars. At 15.0 bars however, the half-life decreased by a factor of 5 for the same temperature change.

Higher activation energies, Ea, for fenamiphos than for fen. sulfoxide (shown in tables 8 to 10) indicate that fenamiphos degradation is more dependent on temperature than fen. sulfoxide degradation. Activation energies for fenamiphos and fen. sulfoxide were similar within fields. Between fields however, Ea of fenamiphos was higher in the Dole than the Del Monte field by a factor of 1.6. Note the large standard errors of the Ea of fenamiphos and fen. sulfoxide from Del Monte field. The small number of observations (6) may be responsible. Since there are no known temperature-related studies on these two compounds, Ea values cannnot be compared with published values.

The best-fit Arrhenius parameters (Ea and A) were subsequently used to predict the effect of a range of field-measured temperatures on fenamiphos and fen. sulfoxide degradation. Comparisons of predicted and field results at two locations from each field showed that the 95% confidence belt of the predicted half-lives readily

overlapped that of the field measured half-lives. The small temperature changes (5°C at Dole and 8°C at Del Monte fields) recorded in the fields represent mostly diurnal fluctuations. The average of the daily maximum and minimum temperatures were almost constant throughout the experimental period; mean temperatures were 24°C and 21°C for Del Monte and Dole fields, respectively. Given the uncertainties related to using the Arrhenius equation for field predictions (as evidenced by large standard errors) and the small temperature fluctuations encountered in the field, we justified using lab data determined from incubation at 23°C and 1.0 bar SMT (0.3 bar SMT for Dole field) for further comparisons of lab with field degradation data. It is important to mention that for cases where temperature fluctuations in the field are much larger, the comparison of lab and field results without temperature correction may not be justified. When such corrections are employed, errors involved in using the best-fit Arrhenius equation from limited lab degradation data for field predictions at a given temperature range must still be critically evaluated with regard to the uncertainties in field measurements.

Overall Comparison of Lab and Field Degradation Data

Initial comparison of the overall lab and field degradation rates summarized in tables 5 to 7 and figures 7 to 9, showed that the degradation rates of fenamiphos and fen. sulfoxide estimated from lab incubation were essentially similar to those measured in the field. Note however, that the overall fenamiphos data set from the Del Monte field gave a poor fit to first-order kinetics (r^2 = 0.61). This is principally attributed to the difference in soil type, since the average fenamiphos degradation rate in the Kolekole soil (locations D,E,F) was lower by a factor of two in comparison with degradation rate from the Kunia soil (locations A,B,C). Sorption measurements were higher by a factor of 1.5 in Kolekole soil as compared with Kunia soil because of the larger amount of organic carbon (see table 3) in the Kolekole soil (Green et al., 1985). Since we have evidence that fenamiphos degradation is retarded when fenamiphos is sorbed at soil surfaces, the lower rate of degradation in the Kolekole soil may be largely attributed to differences in sorption capacity. The effect of soil mineralogy on fenamiphos degradation is unclear and may not be discounted. The effect of soil type in the Del Monte field was not clearly evident in the degradation of fen. sulfoxide; location F had the longest half-life (67 days - average of lab and field).

The overall average CV of fenamiphos half-lives generated from lab and field methods was 15% from the Dole field and 54% from the Del Monte field, whereas the CV of fen. sulfoxide half-lives was 19%. The range of variability is comparable to those reported by Walker and Brown (1983) and Rao et al. (1985). In the former study, degradation rates of simazine and metribuzin were examined on soils sampled from 10 microplots in a 0.64 ha field, whereas the latter study involved measurements of aldicarb TTR and metalochlor on soils collected from 20 locations and four soil depths in a 10 ha field. Degradation experiments in both studies were conducted under controlled lab conditions. Overall CV of simazine and metribuzin was <25% while that that of metalochlor and aldicarb TTR was <30%. Rao et al. (1985) cautioned that the lack of variability in the degradation rates may perhaps be the result of performing degradation experiments under homogeneous environmental conditions in the lab. Although our study involved a small number of locations (six per field), the average CV of the field-measured half-lives (both fenamiphos and fen. sulfoxide degradation from both fields) was consistently larger than the CV for lab-determined values by about 7% (factor of 1.1).

The larger variability in field-measured half-lives is evident from analyses of the variability in measurements of nematicide residues. Overall error for each method can be expressed as the average ratio of the standard error of fraction remaining divided by the fraction remaining, expressed as a percentage. The standard error (shown in tables 11 and 12) of field measurements, was 20% and 8% of the residue for fenamiphos and fen. sulfoxide, respectively. In contrast for lab measurements, overall error was 7% and 4% for fenamiphos and fen. sulfoxide, respectively. The larger error from field residue measurements was mainly attributable to field soil variability and instability in the GC instrument. Reproducibility errors from repeated injections of field soil extracts containing fenamiphos or fen. sulfoxide residues from GC analyses were $\leq$ 10% as compared with scintillation counting error of $\leq$ 5% for lab measurements.

Individual Location and Time-Interval Comparisons of Degradation Data

Differences between lab and field results were consistently insignificant ($P < 0.05$) when degradation rates for each location were compared. Recall however that most of the fenamiphos degradation data from the Dole field deviated from

first-order kinetics with significant zero intercepts. Note also from figure 7 (lab and field) that although the slopes (average k = 0.082 day^{-1}) were similar, the intercept was much larger for field data than for the lab data. This simply means that the fraction of fenamiphos remaining at a given time after application was lower in the lab than in the field. This finding prompted us to analyze the data by comparing the fraction of nematicide remaining determined from both methods at specified sampling times.

Comparisons on this basis (tables 11 and 12) showed that residues of fenamiphos and fen. sulfoxide from the Del Monte field were similar regardless of whether they were measured by lab or field methods. This confirmed the results obtained by performing comparisons based on first-order degradation rates. Fenamiphos residues measured by lab incubation from the Dole field however, consistently underestimated residues measured in the field at all sampling times. However, results by the two methods differed only by a factor of 1.4. This can be considered small because the mean first-order degradation half-lives of lab and field data from all six Dole locations ranged from 6.2 to 9.6 days (table 5). The largest and smallest values, therefore, differ only by a factor of 1.5. In fact, the factor increases to 3.6 when a more appropriate comparison is used in which the maximum difference is based on the range of the 95% confidence intervals rather than on the mean half-lives. Furthermore, in our experiments, only chemical and/or microbiological degradation are assumed to be responsible for nematicide dissipation in the field. Other factors such as substrate concentration effects, possible leaching, and plant uptake of nematicides were not accounted for. Bearing in mind that these additional factors may be operative in the field and also given the large uncertainties in field measured residues, the small differences between fenamiphos residues measured by lab and the insitu method are tolerable, particularly when the ultimate use of the lab data is for relative predictions of persistence in large field-scale environments.

Table 11 Fraction of Initial Fenamiphos Remaining in Dole and Del Monte Fields at Different Elapsed Times

TIME	METHOD	DOLE	DELMONTE
3	LAB	0.456§ (.044†) *	0.673 (.023) ns
	FIELD	0.666 (.076)	0.615 (.061)
7	LAB	0.291 (.016) *	0.449 (.020) ns
	FIELD	0.370 (.051)	0.417 (.047)
14	LAB	0.179 (.009) *	0.330 (.003) ns
	FIELD	0.252 (.033)	0.260 (.130)
21	LAB	0.129 (.001) *	---
	FIELD	0.182 (.052)	

§ average of all six (A to F) locations
† numbers in parenthesis are the standard error of fraction remaining.
ns, * nonsignificant and significant difference, at .05 level, respectively.
--- not determined

Table 12 Fraction of Initial Fen. Sulfoxide Remaining in Del Monte Field at Different Elapsed Times

TIME	METHOD	DELMONTE
14	LAB	0.757§ (.034†) ns
	FIELD	0.717 (.048)
35L/30F††	LAB	0.522 (.015) ns
	FIELD	0.612 (.063)
35L/43F††	LAB	0.522 (.015) ns
	FIELD	0.482 (.053)
56	LAB	0.516 (.034) ns
	FIELD	0.485 (.021)

§ average of all six (A to F) locations
† numbers in parenthesis are the standard error of fraction remaining.
ns nonsignificant difference, at .05 level,
†† 35L/30F time intervals compared at 35 days (lab) and 30 days (field),
35L/43F time intervals compared at 35 days (lab) and 43 days (field).

CONCLUSIONS

Errors related to measurements of the degradation parameter from lab and field methods are often not carefully evaluated. Most of the lab and field degradation data of fenamiphos and fen. sulfoxide nematicides were fit reasonably well by first-order kinetics. The first-order degradation rates determined by both methods were similar. For cases where the fit was not truly first-order, the difference between lab and field measured nematicide residues was within a factor of 1.4. This was considered acceptable given the uncertainties contributed from field soil variability and analytical techniques. Thus, degradation kinetic coefficients and half-lives generated from lab incubation of fenamiphos and fen. sulfoxide are reliable estimates for the purpose of forecasting persistence of these compounds in large field soil environments under pineapple cultivation.

APPENDIX A.

PRELIMINARY SORPTION EXPERIMENTS

A.1 Effect of solution:soil ratios on sorption of Fenamiphos on three soils under sterile conditions

METHOD

Soils - (a) Molokai silty clay loam (Typic Torrox), collected from Dole field 4119, Oahu; airdried moisture content (M) = 4% (weight basis)

(b) Pane silt loam (Typic Dystrandept), collected from Maui Pine 277, Maui; M=17%,

(c) Kolekole silty clay loam (Ustoxic Humitropept), collected from Del Monte 2068, Oahu; M=6%.

Standard batch slurry method performed under sterile conditions was used. Soil equivalent to 2 g. OD basis was sterilized by Co-60 irradiation for 9.5 hours (2.5 Mrads). Radiolabeled fenamiphos mixed with analytical grade fenamiphos was prepared in deionized water and filter sterilized. Apparatus used for filter sterilization included a 50 ml glass syringe, Teflon tape, Nalgene in-line filter holder (Cat. No. 330-4000), Gelman 0.45 µm filter and 250 ml glass bottles. Prior to filter sterilization of fenamiphos solution, the glass bottles were autoclaved and the Nalgene holder was irradiated to achieve sterility. The latter was not autoclaved because the holder is made of polypropylene and thus cannot withstand high heat and pressure; also, the micro-filter placed inside the holder tends to warp when autoclaved and therefore does not provide a good seal. The filter holder can adsorb a certain amount of fenamiphos during filtration; it was found that if a large quantity (at least 400 ml) of fenamiphos solution is passed through, the loss is about 4%; loss of about 15% can result if only 100 ml of fenamiphos solution is used. A similar radiolabeled fenamiphos solution was prepared in 0.01M $CaCl_2$ to study the effect of electrolyte solution (if any) on sorption. Concentrations were 1.5, 5, 15 and 30 µg/ml. Five solution/soil ratios were tested: 2.5, 5, 10, 15, and 20. All solution transfers were performed in a sterile transfer hood. Soil slurry was shaken in 50 ml Teflon tubes with an end-over-end rotary shaker for 24 hrs. After centrifuging, an aliquot of the supernatant was counted. The amount sorbed was assumed to be the

difference between the activity in blank standard and the equilibrated supernatant solution. All other losses by volatilization, degradation or mineralization are assumed negligible and not corrected. The contribution of soil moisture from air-dried soils to the initial fenamiphos solution was corrected. The data were fitted to the logarithmic form of the Freundlich isotherm to obtain the best-fit slope (N) and intercept (K_f). All slopes and intercepts generated from different solution/soil ratios and soils were compared statistically using STAN on the IBM PC.

RSULTS AND DISCUSSION

The results showed that sorption of fenamiphos was not changed when the solution/soil ratio was in the range of 10 to 20 (table 13). In the range of 2.5 to 5 however, fenamiphos sorption was significantly different for all three soils studied. There was a trend of increasing sorption with increasing solution/soil ratio. The slopes(N) of the Freundlich isotherms followed a similar trend for all three soils, i.e. at low (2.5 to 5) solution:soil ratios the slopes were significantly different but at high (5 to 20) solution:soil ratios the slopes were similar. There was a trend of decreasing slopes with increasing solution:soil ratios. The effect of changing the electrolyte solution to $CaCl_2$ did not affect the results. A range of 10:1 and 20:1 is recommended for adsorption-desorption studies utilising the dilution method.

Further experiments were conducted to determine the appropriate equilibrium times to use for three soils at moist and airdried conditions (see Appendix A.2). All experiments assumed that sterility was achieved and that no fenamiphos degradation occurred. Adsorption-desorption measurements under sterile conditions, however, were not attempted because it was determined in later experiments (Cheng-Tseu et al.,1986) that Co-60 irradiation actually enhanced fenamiphos oxidation as compared with unsterilized samples during batch-slurry equilibration. Since fenamiphos is extremely susceptible to both chemical and/or microbiological oxidation, sterile studies may be difficult to attain during long adsorption-desorption studies. Consequently, we decided to

critically evaluate the errors associated with fenamiphos sorption under aerobic, non-sterile conditions (Chapter 1).

Table 13. Fenamiphos Sorption Coefficients (K_f) and Slopes (N) of Frendlich Sorption Isotherms of Kolekole, Molokai and Pane Soils at Different Solution:soil Ratios.

Ratio	K_f			
	Kolekole	Molokai	Pane	Pane ($CaCl_2$)
2.5	4.4	5.7	6.8	6.2
5.0	4.8	6.7	8.6	-
10	5.0	7.2	10.5	9.9
15	5.4	7.1	10.9	-
20	5.4	7.1	11.4	10.7

Ratio	N			
	Kolekole	Molokai	Pane	Pane ($CaCl_2$)
2.5	0.92	0.85	1.04	1.05
5.0	0.88	0.80	0.95	-
10	0.84	0.76	0.88	0.90
15	0.85	0.74	0.85	-
20	0.83	0.76	0.84	0.87

A.2 Determination of equilibration times for sorption of fenamiphos and fen. sulfoxide on field-moist and air-dry soils

METHOD

The batch-slurry method was employed under sterile conditions. Field moist and air-dry soils (see Chapter 2 for description of soils and moisture status) equivalent to 1 g OD weight and 10 ml of radiolabeled nematicide solution were used. Two soils, Molokai silty clay loam and Pane silt loam were used. Soil slurries were shaken on an end-over-end shaker for equilibration times of 0.5, 1, 2, and 5 days.

RESULTS

Fenamiphos Sorption

Fenamiphos sorption on Pane soil increased up to three days (fig. 10). Although there was lower sorption on moist soils during the initial equilibration times (0.5, 1 and 2 days), sorption was similar after three days. Fenamiphos sorption on moist Molokai soil, however, was always lower than that of air-dry soil. Sorption increased up to 5 days for air-dry Molokai soil (fig 11) but decreased after one day on moist soil. SInce the actual amount of fenamiphos was not extracted from either soil or supernatant phases, the quantitative effect of the extent of fenamiphos degradation on sorption in these measurements is not known. Oxidation of fenamiphos to fen. sulfoxide over time would tend to reduce the total amount sorbed (i.e. fenamiphos and fen. sulfoxide) after equilibration of fenamiphos is achieved.

Fen. sulfoxide Sorption

Fen. sulfoxide sorption increased for both Molokai and Pane soil and did not seem to reach equilibrium even after 5 days. (fig. 12 and 13). Extraction of fen. sulfoxide and metabolites from both soil and supernatant showed that < 2% of fen. sulfone was found on the Molokai soil after 5 days. In contrast, < 3% of fen. sulfoxide phenol, < 2% fen. sulfone and about 2 % of an unknown metabolite with an Rf of 0.75 was found on Pane soil after 5 days equilibration. The formation of metabolites less polar than fen. sulfoxide during sorption equilibration may be responsible for the apparent increase in sorption.

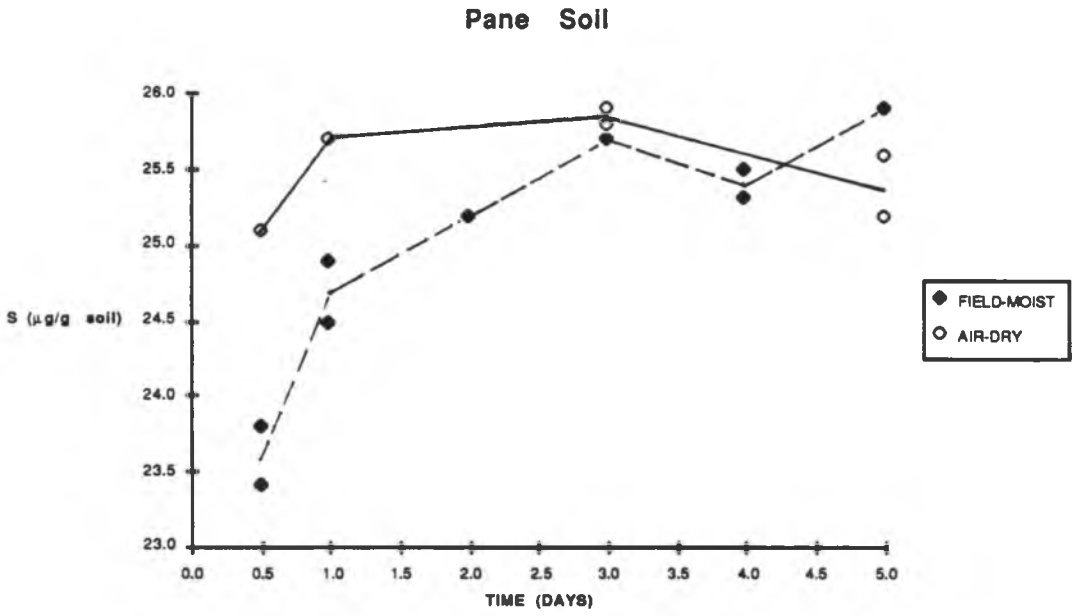

Figure 10 Sorption equilibrium of fenamiphos on Pane soil

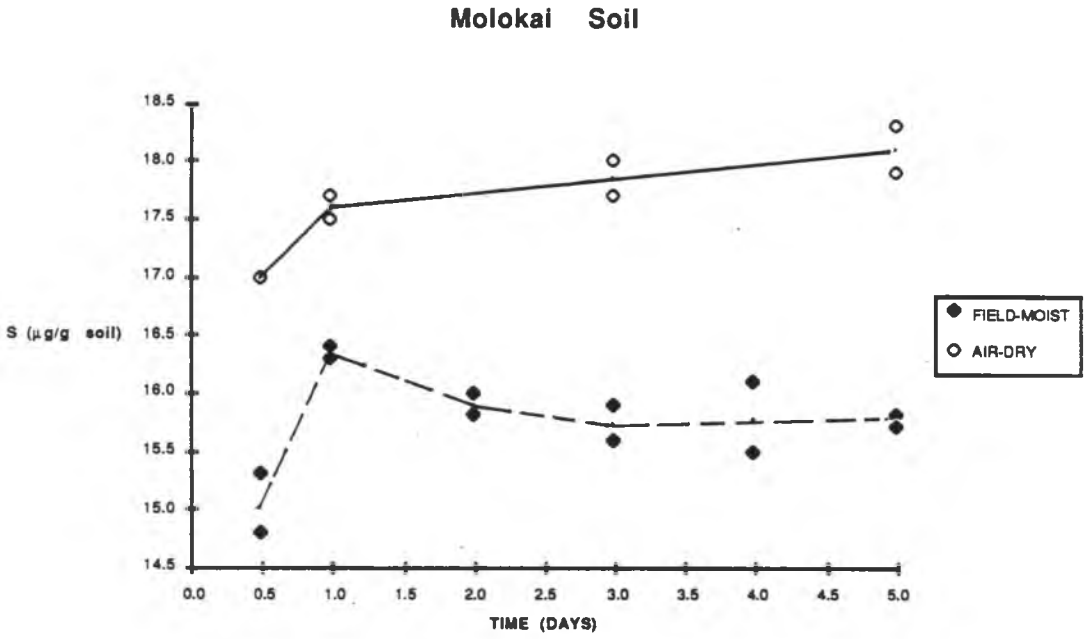

Figure 11 Sorption equilibrium of fenamiphos on Molokai soil

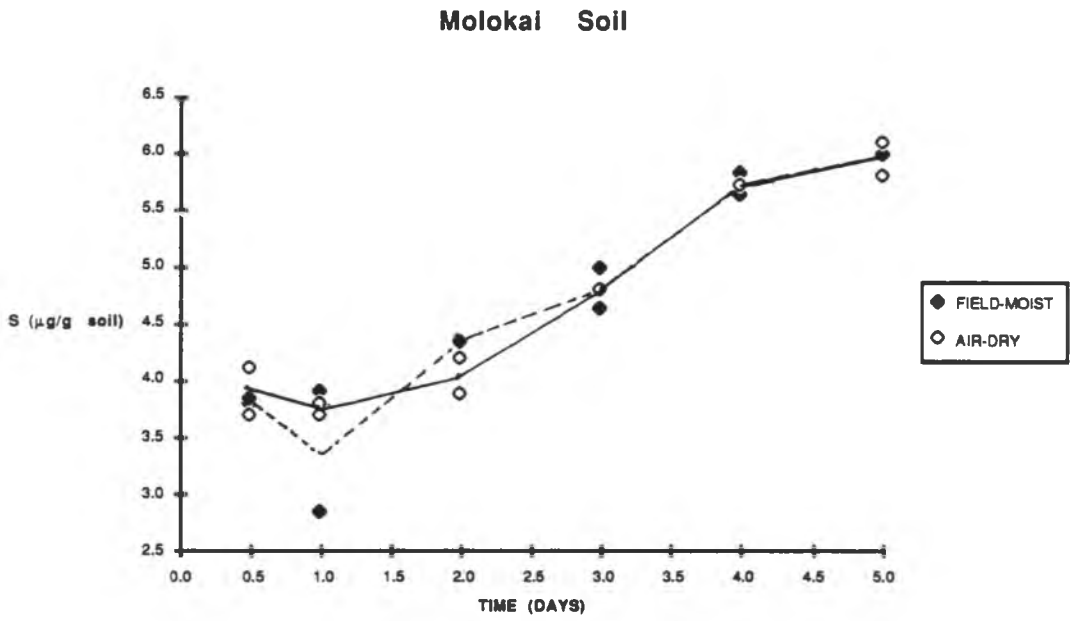

Figure 12 Sorption equilibrium of fenamiphos sulfoxide on Molokai soil

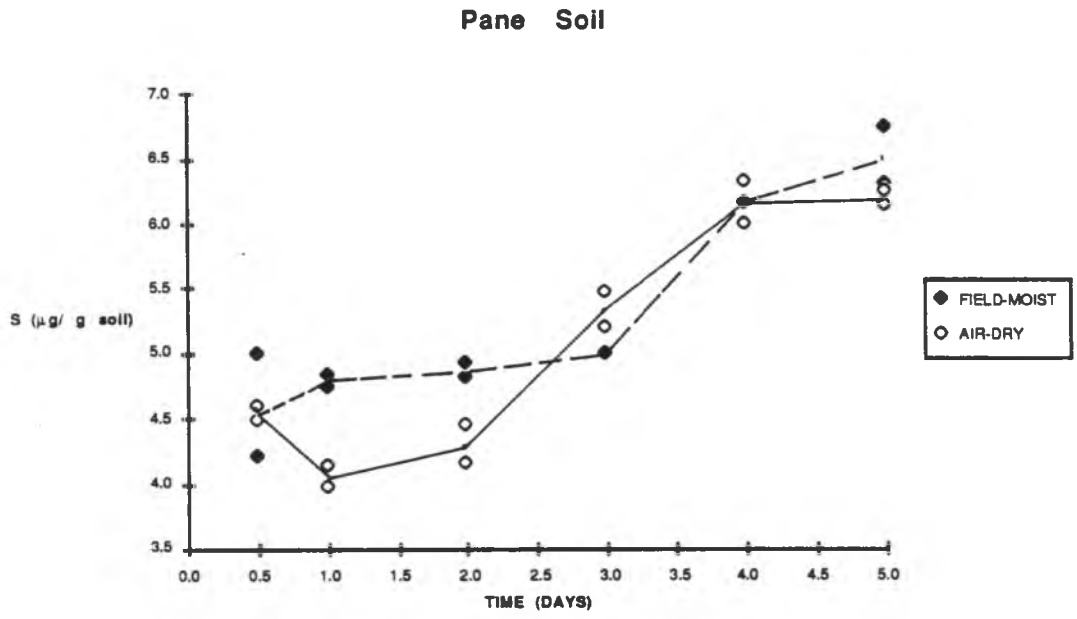

Figure 13 Sorption equilibrium of fenamiphos sulfoxide on Pane soil

A.3 Program to correct for degradation of Fenamiphos during batch equilibration experiments

Method:

A program was written in MS-BASIC (Apple Mac) to correct sorption data for fenamiphos degradation during batch equilibration experiments. Refer to chapter 2 on materiais and methods and fig. 1 on schematic of sorption experiment.

```
' This program corrects the sorption data (amt. sorbed (S) and eqlm. conc. (CE))
'for degradation of the parent compound, Nemacur, during batch equilibration'
'Given:  (1) CI-initial conc.,
'        (2) CE- equilibrium conc.,
'        (3) NMCS- % Nemacur remaining in supernatant
'        (4) NMCSOL- %Nemacur remaining in soil+soil solution


10 DIM CI(6), CE(6),NMCS(6), NMCSOL(6)
40 SOIL   = 1.9962: 'WT. OF OD SOIL
50 MOIST = .1038: ' MOISTURE FROM SOIL
60 TOTVOL = 10.1038 :' TOTAL VOLUME OF SOLUTION PHASE
80 SOILVOL    = 2: ' VOL SOIL SOLUTION EXTRACTED
90 LPRINT "     KD COMPUTATIONS CORRECTED FOR NEMACUR DEGRADATION DURING ADSORPTION EXPT."
100 LPRINT "    ------------------------------------------------------------------- "
110 LPRINT " "
120 LPRINT "      CI       CIADJ      CE      CEADJ       S       SADJ        KD       KDADJ"
130 LPRINT "   (ug/ml)   (ug/ml)    (ug/ml)   (ug/ml)    (ug/g)   (ug/g)     (ml/g)   (ml/g)"
140 LPRINT "    ================================================================================"
150 LPRINT " "
160 FOR N=0 TO 5
170           READ CI(N+1), CE(N+1),NMCS(N+1),NMCSOL(N+1):  ' READ INITIAL,  EQLM CONC, % DEGRA
DATION
180           CIADJ   = (CI(N+1) * 10)/TOTVOL:  ' INITIAL CONC CORRECTED FOR SOIL MOISTURE
190           S          = (CIADJ -CE(N+1))* (TOTVOL/SOIL): ' CAL. AMT. PEST. ADSORBED
200           KD        = S/CE(N+1):                                        ' CAL. DIST. COEEFT
.
210           PSOIL   = S * SOIL :                                          'TOT. AMT. PEST.  I
N SOIL
220           PSOLVOL = CE(N+1) * (SOILVOL + MOIST):        'TOT. AMT. PEST IN SOIL SOLUTION EX
T. WITH SOIL
230           CEADJ = (CE(N+1) * NMCS(N+1):                              'ACTUAL NEMACUR CONC. IN
EQLM SUPERNATANT
240           SADJ  =  ((NMCSOL(N+1) * (PSOLVOL+PSOIL))-(PSOLVOL*NMCS(N+1)))/SOIL: 'ACTUAL NEMAC
UR CONC. IN SOIL PHASE
250           KDADJ = SADJ/CEADJ:     'DIST. COEEFT CORRECTED FOR AMT OF NEMACUR REMAINING (DEGR
ADED)
260           LPRINT  USING "######.###"; CI(N+1), CIADJ, CE(N+1),CEADJ,S, SADJ, KD, KDADJ,
300           LPRINT "     % Nem. in supernatant ="; NMCS(N+1)
310            LPRINT '     %Nem. in soil & soil solution = "; NMCSOL(N+1)
320            LPRINT '  "
321 NEXT  N
322 LPRINT " "
323 LPRINT "      WEIGHT OD SOIL ="; SOIL
330 LPRINT "     MOISTURE FROM SOIL   ="; MOIST
340 LPRINT "     TOTAL VOL OF SOLUTION PHASE="; TOTVOL
360 LPRINT "     VOL OF SOIL SOLUTION EXTRACTED ="; SOILVOL
370 LPRINT "     CI = INITIAL NEMACUR CONC.
380 LPRINT "     CIADJ = INITIAL NEM. CONC CORRECTED FOR SOIL MOISTURE
390 LPRINT "     CE = EQLM CONC OF NEM (+METABOLITES)
400 LPRINT "     CEADJ = EQLM CONC OF NEMACUR (CORRECTED FOR DEGRADATION)
401 LPRINT "     NMCS=% NEMACUR REMAINING IN SUPERNATANT
410 LPRINT "     S = AMOUNT NEM(+METABOLITES) ADSORBED
420 LPRINT "     SADJ = AMOUNT NEMACUR ADSORBED (CORRECTED FOR DEGRADATION)
430 LPRINT "     KD = DIST. COEFFT. OF NEM(+METABOLITES)
440 LPRINT "     KDADJ = DIST. COEFFT OF NEMACUR (CORRECTED FOR DEGRADATION)
441 LPRINT"      NMCSOL =% NEMACUR REMAINING IN SOIL
450 END
```

```
460 DATA  31.028, 15.974, .913  ,  .916
470 DATA  31.028 ,  15.736,  .913,  .916
480 DATA   15.514, 6.861 , .904 ,  .91
490 DATA       4.904 ,  1.916 ,  .824  ,   .914
500 DATA     1.471 ,    .46,    .705 ,   .849
510 DATA 1.471 ,   .455,   .705,  .849
```

Sample Output

KD COMPUTATIONS CORRECTED FOR NEMACUR DEGRADATION DURING ADSORPTION EXPT.

CI (ug/ml)	CIADJ (ug/ml)	CE (ug/ml)	CEADJ (ug/ml)	S (ug/g)	SADJ (ug/g)	KD (ml/g)	KDADJ (ml/g)
31.028	30.709	15.974	14.584	74.583	68.368	4.669	4.688
% Nem. in supernatant = .913							
%Nem. in soil & soil solution = .916							
31.028	30.709	15.736	14.367	75.787	69.471	4.816	4.835
% Nem. in supernatant = .913							
%Nem. in soil & soil solution = .916							
15.514	15.355	6.861	6.202	42.991	39.165	6.266	6.315
% Nem. in supernatant = .904							
%Nem. in soil & soil solution = .91							
4.904	4.854	1.916	1.579	14.869	13.772	7.760	8.723
% Nem. in supernatant = .824							
%Nem. in soil & soil solution = .914							
1.471	1.456	0.460	0.324	5.041	4.349	10.958	13.412
% Nem. in supernatant = .705							
%Nem. in soil & soil solution = .849							
1.471	1.456	0.455	0.321	5.066	4.370	11.134	13.624
% Nem. in supernatant = .705							
%Nem. in soil & soil solution = .849							

WEIGHT OD SOIL = 1.9962
MOISTURE FROM SOIL = .1038
TOTAL VOL OF SOLUTION PHASE= 10.1038
VOL OF SOIL SOLUTION EXTRACTED = 2
CI = INITIAL NEMACUR CONC.
CIADJ = INITIAL NEM. CONC CORRECTED FOR SOIL MOISTURE
CE = EQLM CONC OF NEM (+METABOLITES)
CEADJ = EQLM CONC OF NEMACUR (CORRECTED FOR DEGRADATION)
NMCS=% NEMACUR REMAINING IN SUPERNATANT
S = AMOUNT NEM(+METABOLITES) ADSORBED
SADJ = AMOUNT NEMACUR ADSORBED (CORRECTED FOR DEGRADATION)
KD = DIST. COEFFT. OF NEM(+METABOLITES)
KDADJ = DIST. COEFFT OF NEMACUR (CORRECTED FOR DEGRADATION)
NMCSOL =% NEMACUR REMAINING IN SOIL

Documentation for program to correct sorption data for Fenamiphos degradation.

EQUATION	COMMENTS
CIADJ= (CI X 10)/ TOTVOL	CIADJ = initial conc. of Fenamiphos corrected for soil moisture (µg/ml) TOTVOL = initial volume (10.0 ml) + volume of moisture from soil (ml)
S=(CIADJ-CE) X {TOTVOL)/ SOIL	S = amount of Fenamiphos sorbed (µg/g soil) SOIL = weight of oven-dried soil (g) CE = conc. of Fenamiphos at equilibrium, 4 or 24 hrs (µg/ml)
KD= S/CE	KD = linear partition coefficient (ml/g)
PSOIL= S X SOIL	PSOIL = total amount of Fenamiphos in soil phase (µg)
PSOLVOL = CE X (SOILVOL+MOIST)	PSOLVOL = total amount Feanmiphos in soil solution extracted with soil (µg) SOILVOL = volume of soil solution extracted with soil; 2ml and 3ml for Molokai and Kula soils, respectively (ml) MOIST = moisture from soil (ml)
CEADJ = CE X NMCS	CEADJ = equilbrium conc. corrected for Fenamiphos degradation (µg/ml) NMCS = % Fenamiphos in supernatant
$SADJ = \frac{[NMCSOL \times (PSOLVOL + PSOIL)] - (PSOLVOL \times NMCS)}{SOIL}$	SADJ = amount of Fenamiphos sorbed corrected for Fenamiphos degradation (µg/g soil) NMCSOL = % Fenamiphos in soil phase

A.4 Program to estimate equilibrium concentration from the Freundlich equation

METHOD

From the Freundlich equation:

$S = R(CI - CE) = K_f CE^N$

where S = sorbed phase (µg/g soil),

R = solution/soil ratio (ml/g soil),

CI = initial pesticide concentration (µg/ml),

CE = equilibrium pesticide concentration (µg/ml),

K_f = Freundlich coefficient (ml g^{-1}),

N = constant;

the equilibrium concentration, CE, cannot be solved explicitly. A program was written in MS-Basic (for Apple Mac) to estimate CE by repetitive iterations from the log-transformed Freundlich equation,

$\log [R(CI-CE)] - \log K_f - N \log CE = CONSTANT$

for given values of R, CI, K_f and N. CE is estimated and considered sufficiently accurate when the value of the variable, CONSTANT, is in the region of < 0.002 and > 0.002.

```
'  THIS PROGRAM ESTIMATES THE EQUILIBRIUM CONCENTRATION (CE) FROM THE
'  FREUNDLICH EQUATION, S=Kf X CE^N,  WHERE THE VARIABLES
'  S (=R X (CI-CE)) = SORBED PHASE,
'  R = SOLUTION/SOIL RATIO,
'  CI = INITIAL CONCENTRATION,
'  N = CONSTANT,
'  Kf = FREUNDLICH CONSTANT, ARE KNOWN.
'  THE FREUNDLICH EQUATION IS TRANSFORMED TO THE LOG FORM WHERE
'  LOG (RX(CI-CE)) - LOG (Kf) - (N X LOG (CE) = 0 = CONST.
'  IF THE CONSTANT IS IN THE REGION OF < .002 AND >-.002, THEN
'  THE ESTIMATE OF CE IS CONSIDERED SUFFICIENTLY ACCURATE.

10 READ CI,CE,KF,N,R,I:
20 LPRINT "CI="CI, "CE="CE, "KF="KF, "N="N, "R="R, "I="I:
30 FOR C=0 TO I: ' I=NUMBER OF ITERATIONS
40 CONST=LOG(R*(CI-CE))-LOG(KF)-LOG(CE)*N:
55  IF CONST<-.002 THEN CE=CE-.005
56  IF CONST >.002 THEN  CE=CE+.005
57  IF CONST >-.002 AND CONST < .002 THEN C=I
58  PRINT CE, CONST
90  NEXT C
91  IF CONST <-.002 THEN I=I+100
92  IF  CONST > .002 THEN I=I+100
91  IF CONST <-.002 THEN GOTO 30
92  IF  CONST > .002 THEN GOTO 30
93  S= (CI-CE)*R
94 LPRINT "CONST="CONST,  "CE="CE, "S="S, "I="I
95  END:
100 DATA 2.5, 2,  1,  0.7,  5,  300
```

```
CI= 2.5        CE= 2          KF= 4          N= .7          R= 5
```

```
CI= 5          CE= 3          KF= 4          N= .7          R= 5
CONST= .00059318161835        CE= 3.195      S= 9.025       I= 300
```

```
CI= 10         CE= 8          KF= 4          N= .7          R= 5
CONST=-.0017641042218         CE= 6.91       S= 15.45       I= 300
```

APPENDIX B

PRELIMINARY DEGRADATION EXPERIMENTS

B.1 Preliminary experiment on comparing laboratory and field degradation rates of fenamiphos at two locations at Dole 4119 using the bottle technique

METHOD

Field

Two 50 m pineapple beds were selected in a research area at Dole field 4119. One of the bed was a normal 4 year old pineapple bed (named inbed plot) in its second ratoon stage and the other was a fallow area (named bare plot) immediately adjacent to the normal bed. Monitoring of soil temperature was conducted on both bare and inbed plots with soil temperature probes connected to a Campbell micrologger for continuous input every hour. Probes were placed at various depths and also inside a bottle (which was buried in the bed) to check for temperature changes actually occurring in the bottle where the nematicide is expected to be present. Soil temperature probe 1 was placed at a soil depth of 5 cm at the beginning of the inbed plot. Probe 2 was placed at the same depth but about 25 m away in the plot. Probe 3 was set up to check for temperature inside the bottle as compared with insitu soil temperature. It was therefore placed inside the bottle filled with soil and buried at the same position as probe 2. Unfortunately, the micrologger was flooded during the preliminary experiment. Later, soil temperature was monitored by instantaneous soil temperature probes and by max/min thermometers. They did not provide continuous monitoring of soil temperature in the field but the data obtained were probably sufficient.

Soil moisture was monitored by taking surface samples in the bed and also by removing a few buried bottles (with soil).. The samples were brought to the laboratory and soil moisture samples from the bottles were removed every 2.5 cm to check for moisture equilibrium between the surrounding soil and soil inside the bottle.

Soil samples (0-15 cm) were taken in the beds and brought back to the laboratory to be coarse sieved (5 mm opening) and partially air-dried. Field moist samples from both beds were 30% (by weight) at sampling. After partially air-drying in the lab, the moisture content was 20% and an exact amount of fenamiphos solution was added to bring the airdried samples to field moist conditions

(i.e. 30%). Partially airdried soils were dosed with e.c. (emulsifiable concentrate) grade fenamiphos (10 µg /g OD soil) with a fast delivery 25 ml pipette, mixed thoroughly and then put into wide-mouth bottles (6 x10 cm). The top was covered with a piece of muslin cloth and tied securely around the neck with rubber bands. The bottles filled with treated soil were then taken out to the field and installed in the beds (see schematic, fig 14). The time between sampling of the soils to re-installation of bottles with treated soils was 3 days. At the time of installation, the field was rather wet (42% and 46% for bareplot and inbed plot, respectively). It had rained heavily three days after soil sampling. Sampling times were 0, 3, 9, 15, 30 days after treatment. At each sampling time, relicate bottles were removed from each bed, placed in coolers and brought to the lab for extraction the same day. Refer to Chapter 3 (extraction and analyses section) for details on GC analyses. Soil temperature and moisture were monitored periodically during the experiment.

Laboratory

The standard C-14 method of dosing soils and incubation in culture tubes were used. Soils from the inbed plots were used. Additionally, soils treated with e.c. fenamiphos and placed in bottles were incubated in the lab. together with the radiolabeled samples. Soil moisture tensions were set at 0.1, 0.3 and 1.0 bar. Only ambient temperature (23 C) was used. Sampling times were the same as the field setup.

RESULTS AND DISCUSSION

Table 14 Degradation Half-lives of Fenamiphos from Field and Laboratory Experiments

DESCRIPTION	GRADE	HALF-LIFE
FIELD (INBED)	E.C.	10.3
FIELD (BAREPLOT)	E.C.	9.3
INLAB	E.C.	10.2
INLAB- 0.1BAR	14C	8.2
INLAB- 0.3BAR	14C	8.5
INLAB- 1.0BAR	14C	8.2

Soil Temperature

Soil temperature inside the bottle (probe 3) was generally higher than the insitu soil temperature (probe 2) by only about 1 C in the afternoons. The difference in the insitu soil temperatures (probes 1 and 2) was also about 1 C. The average temperature however, was very similar. Consequently, the soil temperature in bottles buried in the surface bed is representative of insitu soil temperature (fig. 15).

Soil Moisture

Soil moisture inside the bottle also showed similar moisture regimes as the insitu soil moisture. Only at higher insitu soil moistures (>39%, particularly after heavy rains), more time (maybe a few days) is needed for moisture equilibration.

Degradation

Degradation rates (half-lives of 10.3 days) were the same for both laboratory and field data using e.c. fenamiphos (table 14). There was no significant effect of soil moisture (0.1 -1.0 bar) on fenamiphos degradation in the laboratory. Laboratory degradation using C-14 fenamiphos, underpredicted the field degradation by about 2 days; only the 1.0 bar treatment however, was significantly different from the field data. Although the preliminary experiment was successful, there were some concerns and problems raised by various researchers;

(1) Because the field samples were brought to the laboratory and manipulated (such as partially airdrying and rewetting) and later placed in bottles buried in the field, degradation in the field bottles may not represent field conditions;

(2) lack of aeration in the bottles may prevent the bottle technique from adequately representing field conditions;

(3) the bottle technique was very labor intensive.

A better, slightly modified insitu method of measuring nematicide degradation was thus developed and used in the subsequent field degradation experiments.

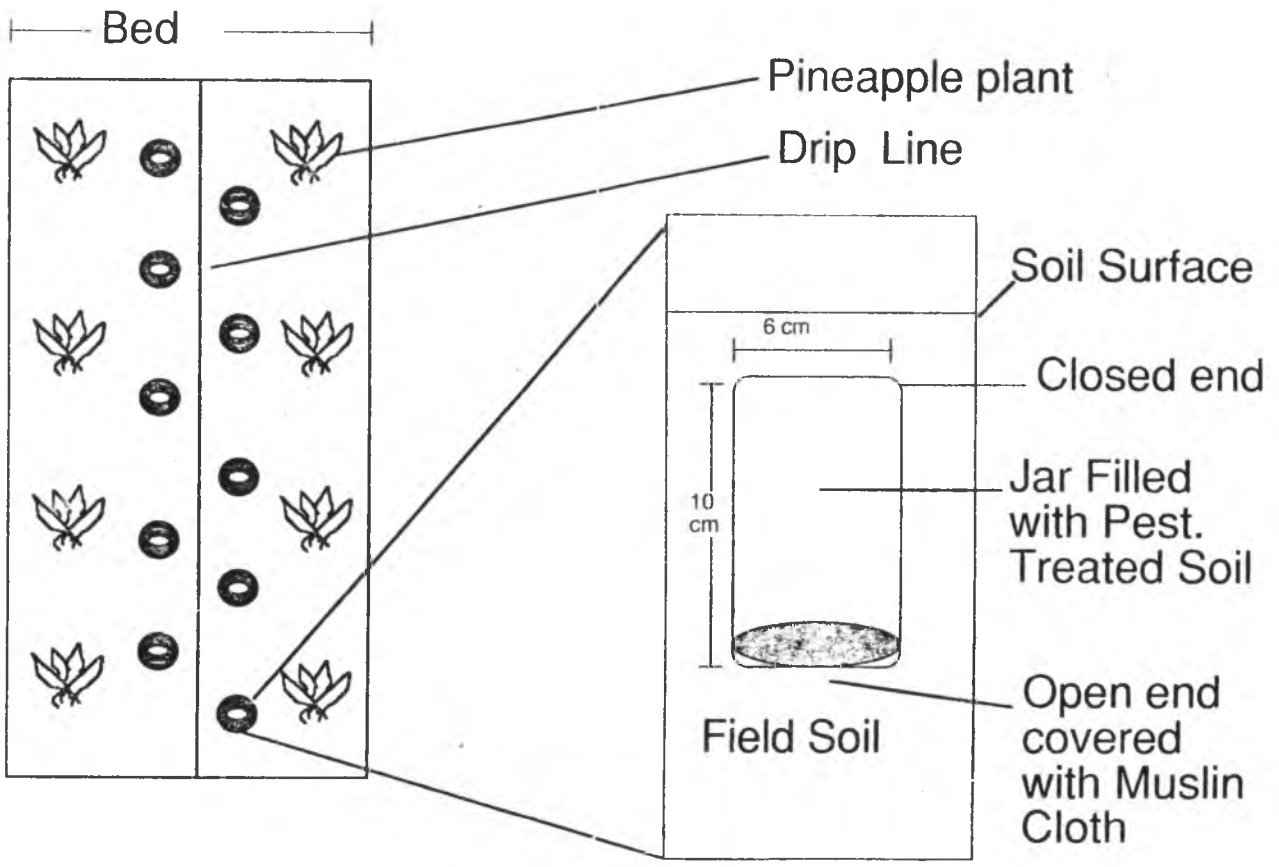

Figure 14 Schematic of preliminary field degradation experiment

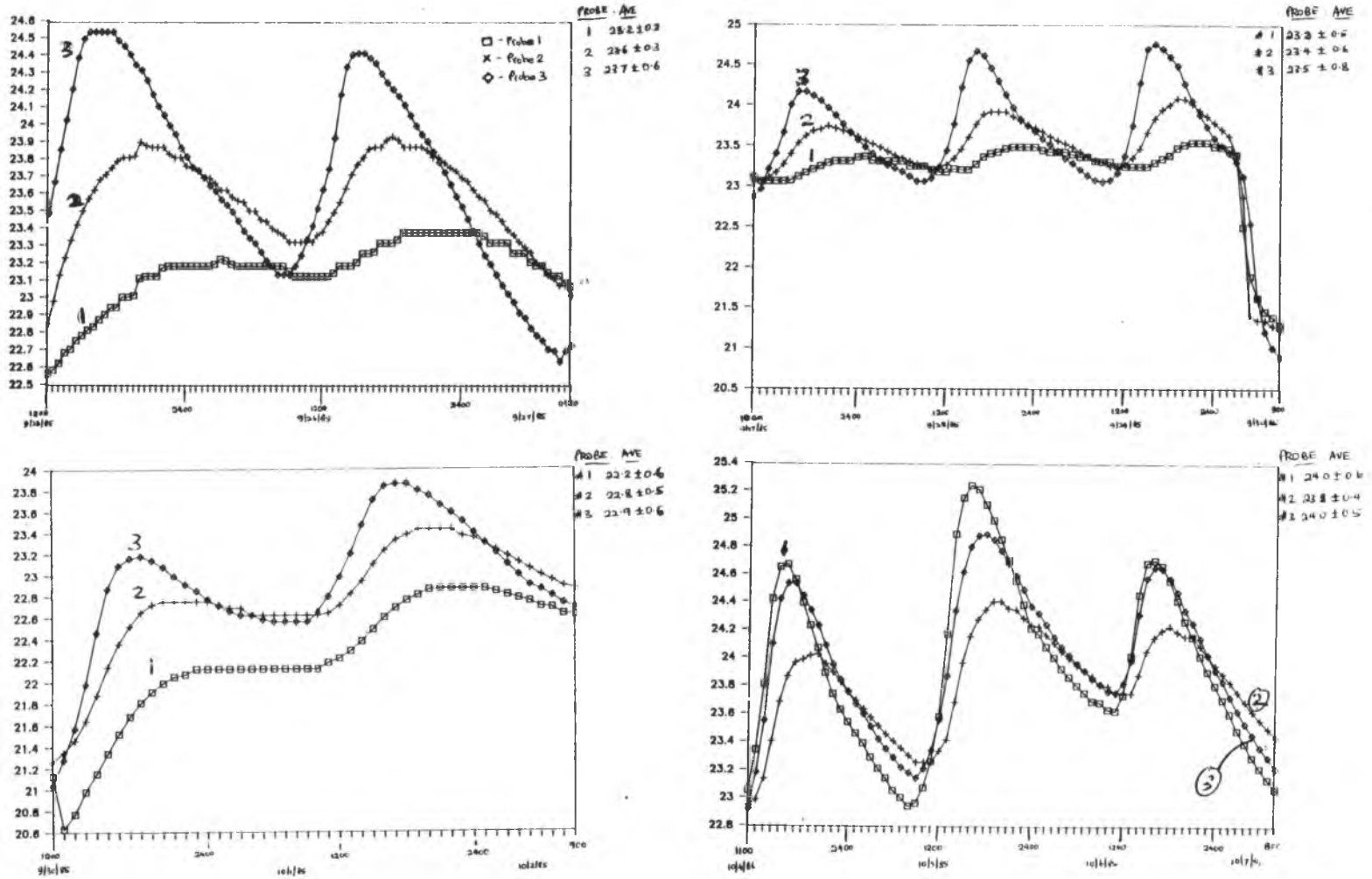

Figure 15 Temperatures of surface soils recorded at Dole 4119 field

B.2 Determination of depth of leaching of fenamiphos and fen. sulfoxide in field soils contained in aluminum cylinders

METHOD

1. Aluminum cylinders containing surface field soils (refer to chapter 2 for details of experiments) from at least three locations from Dole and Del Monte fields were excavated and brought to the laboratory.
2. Different amounts of C-14 fenamiphos or fen. sulfoxide were carefully dripped on the soil surface and allowed to infiltrate into the core.
3. Four hours after nematicide application, layers of soil in increments of about 3 cm were removed. Each layer of soil was weighed, mixed, and a subsample was taken to be extracted with acetone (4:1 solvent/soil ratio). The extract was rotoevaporated to reduce the volume, transferred to 20 ml centrifuge tubes, and an aliquot was radioassayed. The acetone extract was not subjected to TLC to separate the metabolites. Thus, the radioactivity represents total toxic residues. The recoveries of radioactivity ranged from 75% to 85%. The percentage of recovered residue at each depth increment (table 15) was adjusted for the total recovery percentage for the core.

RESULTS AND DISCUSSION

1. An equation to predict nematicide leaching ,

$d = V/(\theta_{fc} \times R)$, where $R = [\,1 + (\rho K_d/\theta_{fc})]$,

θ_{fc} = volumetric moisture content in soil from field(cm^3/cm^3),

V = volume of solution applied/surface area (cm),

ρ = bulk density (g/cm^3)

Kd = adsorption distribution coefft. (cm^3g^{-1})

d = depth of penetration (cm).

generally underpredicted the depth of leaching. Preferential flow in large pore channels was probably responsible for the underprediction. Aqueous nematicide solution volumes of 25 ml and 10 ml of fenamiphos and fen. sulfoxide respectively, were found to be appropriate for minimizing loss of nematicide from the soil in the aluminum cylinder by leaching.

Table 15 Depth of nematicide leached for different soils at various locations from Dole and Del Monte fields

Nematicide	Field	Site	Depth (cm)	% of Recovered Residue In Each Depth Increment
Fenamiphos	DOLE4111	A	0-2	85.1
			2-4	14.8
			4-6	0.1
			6-8	ND
			8-10.5	ND
		B	0-2	93.3
			2-4	6.7
			4-6	ND
			6-8.5	ND
		C	0-2	93.2
			2-4.5	4.7
			4.5-6	1.4
			6-8	0.3
			8-10.5	ND
Fenamiphos	DM2068	C	0-3	91.5
			3-7	8.1
			>7	0.4
		D	0-3.5	98.4
			3.5-7	1.6
			>7	ND
		F	0-3	81.7
			3-6	10.5
			>6	7.8 §
Fen. Sulfoxide	DM2068	A1*	0-5	99.5
			5-8	0.5
			>8	ND
		A2	0-4.5	92.6
			4.5-8	7.3
			>8	ND
		F1	0-5	74.8
			5-8	19.6
			>8	5.6 §
		F2	0-5	98.2
			5-8	1.8
			>8	ND

ND not detectable

* 1,2 denotes replicate core samples

§ possible contamination from soil samples taken above depth increment

B.3 Temperature and moisture regimes recorded at Dole and Del Monte fields during degradation experiments

METHOD

Temperature was recorded by instantaneous Cole Parmer temperature probes and Taylor max/min thermometers. Two temperature probes were installed in the 0-10 cm soil surface at each location. Two max/min thermometers were similarly installed only at specific locations: A and D locations at Dole fields and A and F locations at Del Monte fields. Temperatures were recorded every 2 to 3 days.
The majority of the readings were obtained in the morning (9-10 am) but some were obtained in the early afternoon (2-3 pm).

RESULTS AND DISCUSSION

Temperature

Temperatures recorded from max/min thermometers were consistently higher than temperatures recorded from temperature probes by an average of 1.7 C. Under lab ambient conditions however, the difference between temperature probe readings and glass thermometers (Fisher) was $\pm$ 2 C. Thus, no corrections were made on temperatures readings obtained from max/min thermometers. The range of temperatures recorded (tables 16, 17, 18) in the three field experiments were 19-24 C (Dole.F), 20-28 C (Del Monte.F), and 22-30 C (Del Monte.fen. sulfoxide). These field temperature ranges were used as inputs in the best-fit Arrhenius equation generated from lab experiments (refer to Chapter 4 for detaiis) to evaluate the impact of field temperature fluctuations on fenamiphos and fen. sulfoxide degradation.

Moisture

Soil moisture content in cores at all locations rapidly redistributed after three days to SMT corresponding to about 0.3 bar and 1.0 bar at Dole and Del Monte fields, respectively (figs. 16 to 20). The relationship between soil moisture (by weight) obtained from field core samples (figs. 16 to 18) and SMT can be obtained from the soil moisture characteristic curve (figs. 19 and 20). Soil moisture characteristic curves were determined in the lab on soils collected from specific field locations from Dole and Del Monte fields. Because of the small fluctuations in soil moisture and also the fact that there is no significant effect of soil moisture on fenamiphos and fen.

sulfoxide degradation, lab degradation data determined at a fixed SMT were used to compare with field degradation data.

Table 16 Soil temperature recorded at Del Monte 2069 - fen.sulfoxide experiment

TIME	A	A1	AMX	AMN	B	C	D	E	F	F1	FMX	FMN
0	23.4	24	30	21	23.2	23.2	23.6	23.2	23.2	25	31	20
3	23.6	25	28	22	23.5	23.5	24.5	23.8	23.6	26	29	22
4	23.3	25	28	22	23.2	23.2	24.5	23.8	23	25	28	23
19	23.6	25	29	22	23.7	23.8	24.5	23.6	23.6	26	30	21
20	23.8	25	30	23	23.8	23.8	24.5	23.6	23.5	26	30	21
28	24.2	26	31	22	24.5	24.4	25.8	24.5	24.4	28	32	21
33	23.6	24	29	23	23.3	23.3	23.5	22.9	23.1	25	30	23
41	25.6	28	29	22	25.4	25.5	26.6	25.5	24.9	29	32	22
46	23.9	25	30	23	24	24.2	25	24.2	24	27	33	25
DIFF	1.2								2.6			
AVG	23.88	25.	29.	22.	23.8	23.8	24.7	23.9	23.7	26.	30.	22
STD	0.655	1.1	0.9	0.6	0.67	0.70	0.92	0.72	0.59	1.3	1.4	1.4

TIME - DAYS AFTER NEMATICIDE APPLICATION
A TO F - INSTANTANEOUS TEMP PROBE READINGS FROM SITES IN FIELD
A1, F1 - INSTANTANEOUS TEMP READINGS FROM MAX/MIN THERMOMETERS AT SITES A1 AND F1

AMX,AMN- MAX AND MIN TEMP FROM MAX/MIN THERMOMETERS AT SITE A
FMX,FMN- MAX AND MIN TEMP FROM MAX/MIN THERMOMETERS AT SITE F
AIR - AIR TEMPERATURE FROM TEMPERATURE PROBE IN SHADED CANOPY
DIFF - AVERAGE DIFFERENCE BETWEEN TEMP READING FROM PROBE AND MAX/MIN THERMOMETER
AVG - AVERAGE TEMPERATURE
STD - STANDARD DEVIATION

Table 17 Soil temperature recorded at Del Monte 2068 - fenamiphos expt

TIME	A	A1	AMX	AMN	A2	A2MX	A2MN	B	C	D	E	F	F1	FMX	FMN
0	22.7	23	24	21	24	27	22	23	22.5	23	22.4	24	26	26	22
3	22.3	24	28	22	22	24	20	22.9	22.2	22.5	21.8	22.4	25	28	22
4	22.2	22	24	20	23	27	21	22.3	22.1	22.1	21.7	22.2	24	27	21
7	22.3	23	24	21	25	28	22	22.3	22.7	21.9	22.1	23.1	26	29	21
11	24.3	28	29	19	29	29	21	26.6	24.5	26.4	25.6	26.2	28	28	20
14	23	22	31	20	25	31	22	22.7	23.6	23.8	22.7	22.9	24	30	21
15	23	23	30	21	25	30	23	23.3	22	23.4	22.4	22.6	24	30	21
17	22.8	23	30	19	25	30	21	22.6	22.2	23.3	23	23	24	26	20
21	21.6	24	30	18	23	28	21	21.2	20.7	21.8	21.7	21.4	23	28	19
DIFF	1.2											1.8			
AVG	22.68	23.	27.	20.	24	28.	21.4	22.9	22.5	23.1	22.6	23.0	24.	28	20.
STD	0.709	1.7	2.7	1.1	1.	1.9	0.83	1.39	1.00	1.33	1.14	1.28	1.4	1.4	0.9

TIME - DAYS AFTER NEMATICIDE APPLICATION
A TO F - INSTANTANEOUS TEMP PROBE READINGS FROM SITES IN FIELD
A1, F1 - INSTANTANEOUS TEMP READINGS FROM MAX/MIN THERMOMETERS AT SITES A AND F
AMX,AMN- MAX AND MIN TEMP FROM MAX/MIN THERMOMETERS AT SITE A
FMX,FMN- MAX AND MIN TEMP FROM MAX/MIN THERMOMETERS AT SITE F
AIR - AIR TEMPERATURE FROM TEMPERATURE PROBE IN SHADED CANOPY
DIFF - AVERAGE DIFFERENCE BETWEEN TEMP READING FROM PROBE AND MAX/MIN THERMOMETER
AVG - AVERAGE TEMPERATURE

STD - STANDARD DEVIATION

Table 18 Soil temperature recorded at Dole 4111 - fenamiphos expt.

TIME	A	A1	AMX	AMN	B	C	D	D1	DMX	DMN	E	F	AIR
0	20.4	21	21	19	20.4	21.2	21.6	23	23	18	21.3	20.8	
3	21	22	24	19	21	21.5	21.8	22	25	18	21.3	21.6	27.5
4	20.8	21	24	21	20.7	21.2	21	21	24	18	21.1	20.9	25.4
7	20	20	24	19	19.6	20.5	20.1	20	23	18	19.8	19.8	24.1
11	20.1	21	24	19	20.4	20.3	20.4	21	24	18	20.7	20.5	28.3
14	20.1	21	24	19	20.2	20.4	20.3	21	23	18	20.9	20.5	27.6
21	21.6	23	27	20	21.5	22	22	23	26	18	22	22.4	30.1
DIFF	0.7							2.4					
AVG	20.57	21.	24	19.	20.5	21.0	21.0	21.5	24	18	21.0	20.9	27.1
STD	0.546	0.8	1.6	0.7	0.56	0.58	0.72	1.04	1.06	0	0.62	0.78	1.94

TIME - DAYS AFTER NEMATICIDE APPLICATION
A TO F - INSTANTANEOUS TEMP PROBE READINGS FROM SITES IN FIELD
A1, D1 - INSTANTANEOUS TEMP READINGS FROM MAX/MIN THERMOMETERS AT SITES A AND D
AMX,AMN- MAX AND MIN TEMP FROM MAX/MIN THERMOMETERS AT SITE A
FMX,FMN- MAX AND MIN TEMP FROM MAX/MIN THERMOMETERS AT SITE F
AIR - AIR TEMPERATURE FROM TEMPERATURE PROBE IN SHADED CANOPY
DIFF - AVERAGE DIFFERENCE BETWEEN TEMP READING FROM PROBE AND MAX/MIN THERMOMETER
AVG - AVERAGE TEMPERATURE
STD - STANDARD DEVIATION

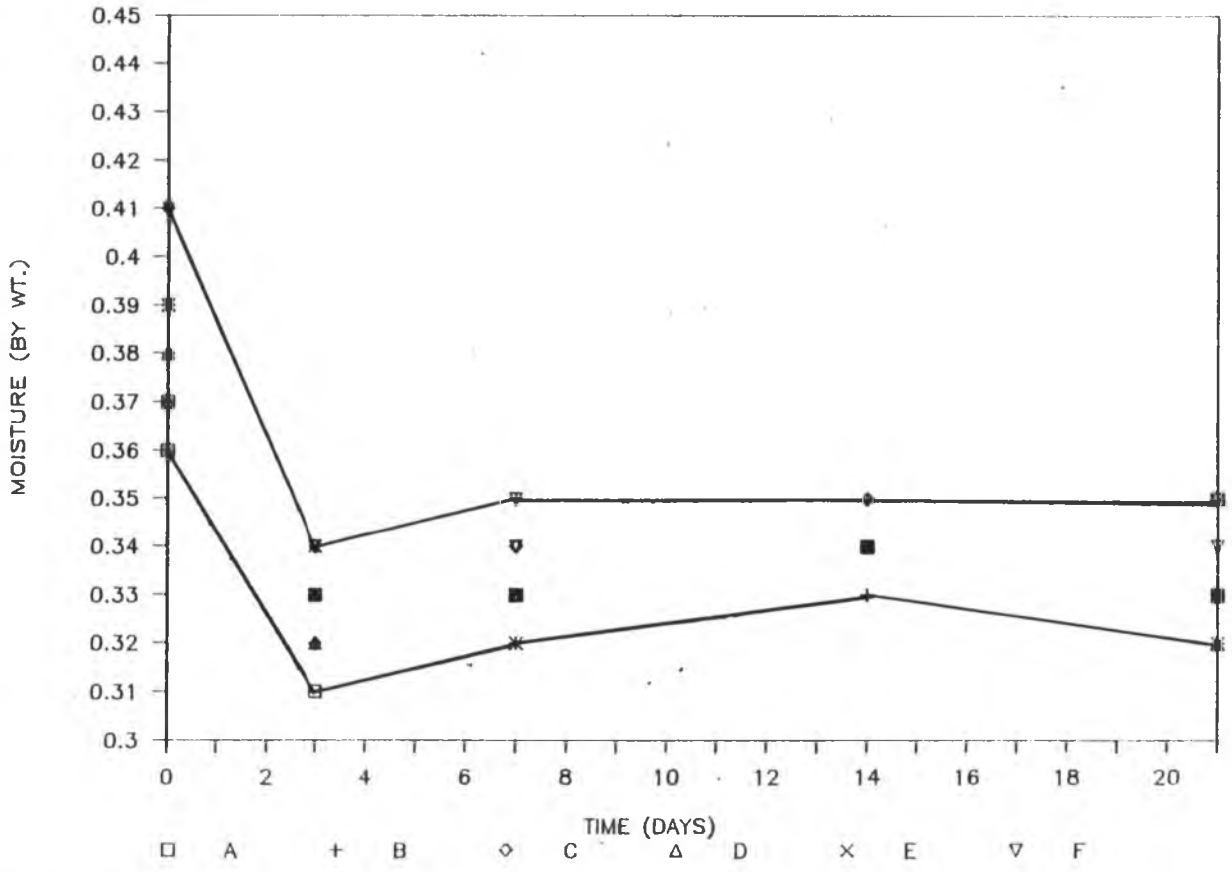

Figure 16 Moisture distribution of soils from Dole-fenamiphos experiments

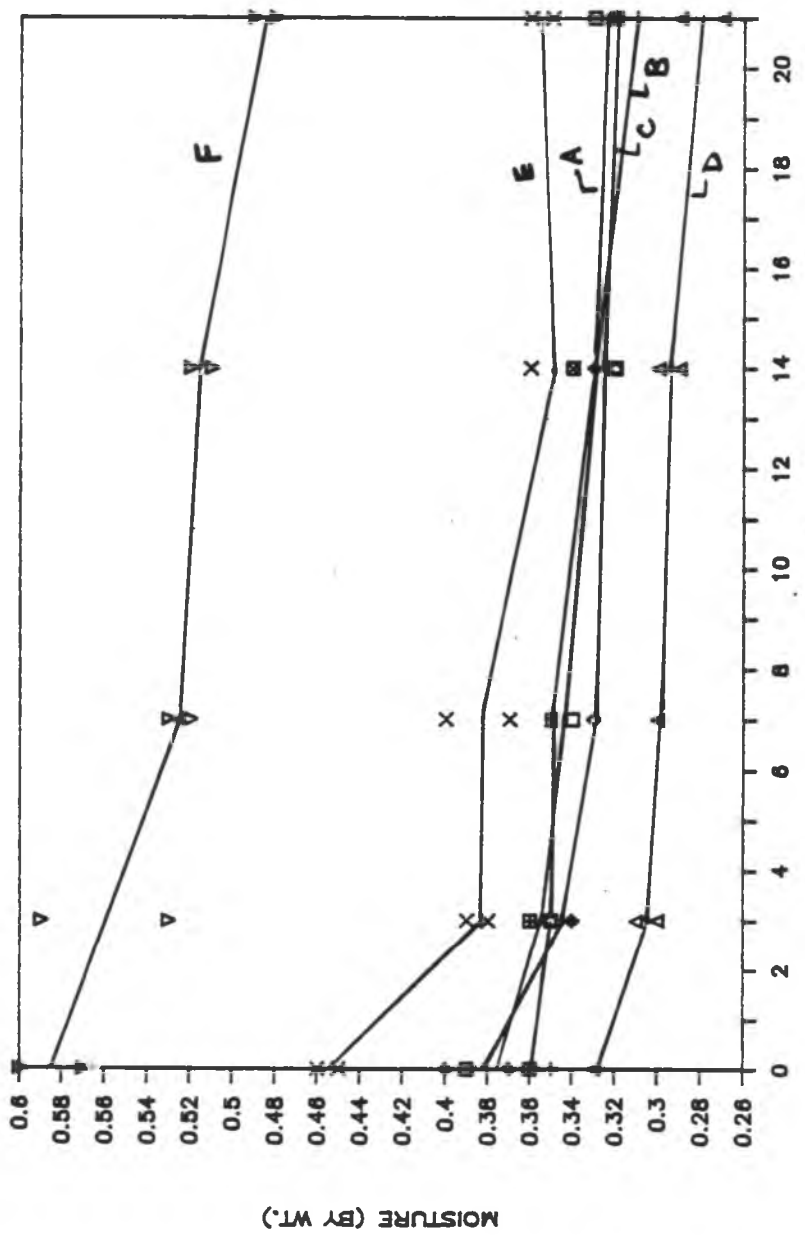

Figure 17 Moisture distribution of soils from Del Monte-fenamiphos experiments

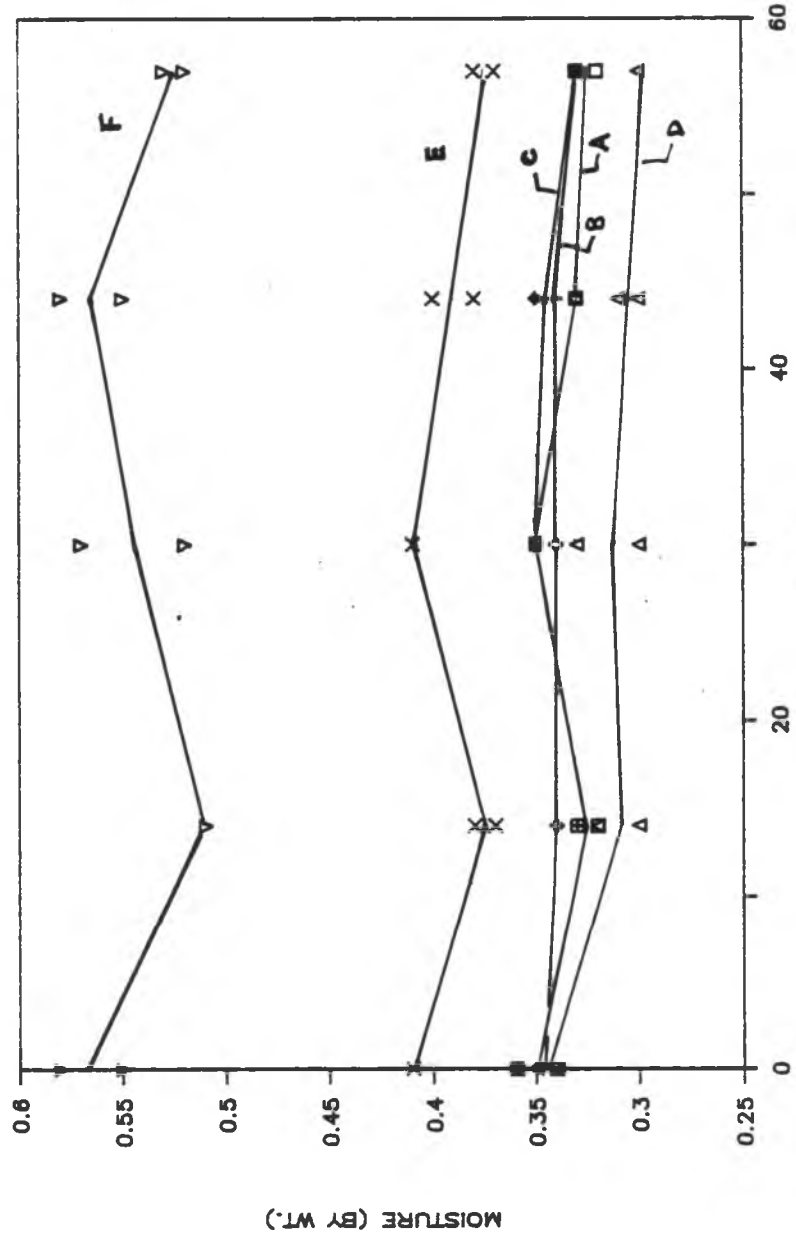

Figure 18 Moisture distribution of soils from Del Monte-fen. sulfoxide experiments

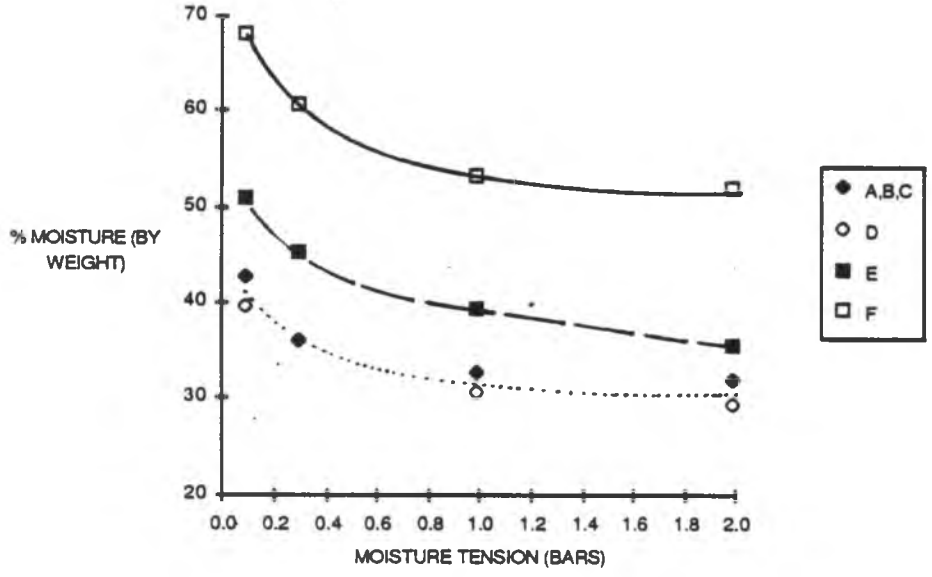

Figure 19 Soil moisture characteristic curves of soils from Del Monte 2068 field

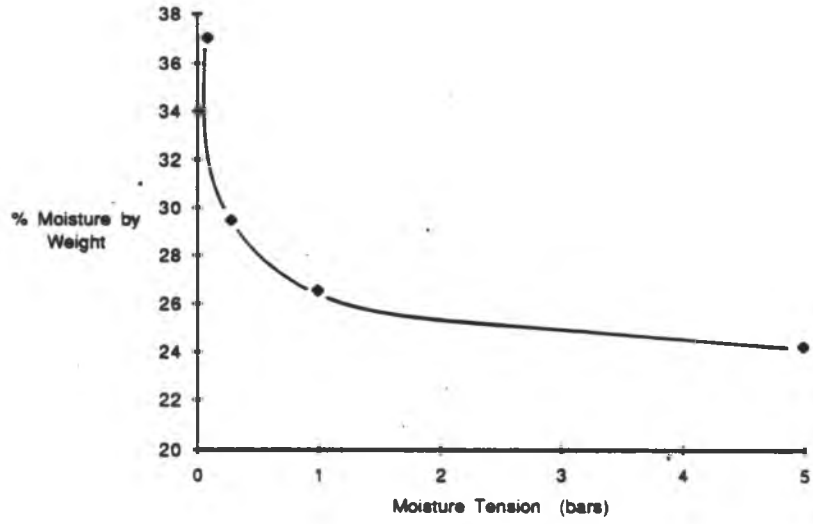

Figure 20 Soil moisture characteristic curve of selected soils (locations A, C, F) from Dole 4111 field

B.4 Effect of three concentrations on degradation of fenamiphos and fen. sulfoxide in the laboratory

METHOD

A lab incubation experiment was set up to detrermine the effect of a range of concentrations on the degradation of fenamiphos and fen. sulfoxide in soils collected from Dole and Del Monte fields. This experiment was necessary in view of the possibility that there is a non-uniform distribution of nematicides in the field experiments (see Appendix B.2). Soils collected from two locations (A and F) from Del Monte field and only one location (A) from Dole field were used (see soil description in Chapter 3 for details). Three concentrations ranging from 1.5 to 10 µg/g soil for fenamiphos and 3 to 18 µg/g soil for fen. sulfoxide were utilized. Soils were incubated at 23 C and 1.0 bar SMT.

RESULTS AND DISCUSSION

There was no effect of concentration (table 19) on degradation of fenamiphos and fen. sulfoxide on soils from Dole field. In Del Monte soils however, there was a trend of increased persistence at higher concentrations of fenamiphos and fen. sulfoxide. Comparisons of degradation half-lives between the highest and lowest concentration of fenamiphos and fen. sulfoxide showed that (a) the difference was by a factor of 1.4 on soils from location A and (b) the difference was by a factor of 1.7 on soils from location F. When the first-order degradation rates were compared statistically, there was no significant difference between concentration treatments.

Table 19 Effect of concentration on fenamiphos and fen.sulfoxide degradation

I.D.	K	STDERR	UPPER	LOWER	TO.5	SE	UPPER	LOWER	b	R-2
DAH.f	0.1192	0.00819	0.138	0.099	5.81	0.399	6.759	4.869	.07ns	0.991
DAM.f	0.1414	0.01433	0.175	0.107	4.90	0.496	6.076	3.726	.13ns	0.979
DAL.f	0.1633	0.03790	0.252	0.073	4.24	0.984	6.573	1.915	.335ns	0.903
DFH.f	0.09434	0.00858	0.114	0.074	7.34	0.667	8.925	5.766	.09ns	0.984
DFM.f	0.1125	0.00949	0.134	0.090	6.16	0.519	7.390	4.931	.09ns	0.986
DFL.f	0.1483	0.02863	0.216	0.080	4.67	0.902	6.807	2.539	.256ns	0.931
MAH.f	0.1397	0.03206	0.215	0.063	4.96	1.138	7.653	2.269	.204ns	0.945
MAM.f	0.1351	0.02023	0.182	0.087	5.13	0.768	6.947	3.313	.181ns	0.957
MAL.f	0.1393	0.03645	0.225	0.053	4.97	1.301	8.053	1.897	.351ns	0.88
DAH.s	0.02376	0.00520	0.036	0.011	29.1	6.377	44.24	14.07	.04ns	0.954
DAM.s	0.02363	0.00613	0.038	0.009	29.3	7.615	47.34	11.31	.05ns	0.937
DAL.s	0.03064	0.00512	0.042	0.018	22.6	3.784	31.56	13.66	.04ns	0.973
SFH.s	0.01902	0.00584	0.032	0.005	36.4	11.17	62.86	9.994	.05ns	0.914
SFM.s	0.02363	0.00214	0.028	0.018	29.3	2.655	35.61	23.05	.02ns	0.992
SFL.s	0.03308	0.00429	0.043	0.022	20.9	2.720	27.38	14.51	.03ns	0.984

K - first-order rate coefficient
STDERR - standard error of K
UPPER, LOWER - 95% upper and lower confidence limits of K or TO.5
TO.5 - half-life
SE - standard error of TO.5
b - intercept
ns, * - nonsignificant and significant difference of intercept from 0, respectively
R-2 - coefficient of determination of fit of degradation data to first-order kinetics

M - DOLE FIELD 4111
D - DELMONTE FIELD 2068
A,F - SITES IN FIELD
H.f - FEN. CONC 10 UG/G SOIL
M.f - FEN. CONC 5 UG/G SOIL
L.f - FEN. CONC 1.5 UG/G SOIL
H.s - FENSO. CONC 18 UG/G SOIL
M.s - FENSO. CONC 9 UG/G SOIL
L.s - FENSO. CONC 3 UG/G SOIL

B.5 Effect of three sampling times on degradation of fenamiphos on soils collected from Dole 4119.

METHOD

The effect of temporal variability on fenamiphos degradation was studied at Dole 4119 (field where preliminary degradation experiments were conducted by the bottle technique, refer to appendix B.1). Soils were sampled from the surface 0-15cm in the pineapple bed at the following times: Nov.86, March 87 and June 87. Standard radiolabeled fenaniphos experiments were conducted.

Results and Discussion:

These experiments were inconclusive because too few sampling times were used (table 20).

Table 20 Effect of time of soil sampling on fenamiphos degradation

I.D.	K	STDERR	UPPER	LOWER	TO.5	SE	UPPER	LOWER	b	R-2
11.1.85	0.05609	0.00931	0.078	0.033	12.3	2.050	17.37	7.338	0.59	0.838
11.1.85	0.05781	0.00881	0.079	0.036	11.9	1.826	16.45	7.517	0.52	0.878
11.1.85	0.06143	0.00738	0.079	0.043	11.2	1.356	14.60	7.963	0.49	0.908
3.5.86	0.09880	0.01193	0.127	0.070	7.01	0.847	9.018	5.011	.34ns	0.907
3.5.86	0.08115	0.01046	0.105	0.056	8.53	1.100	11.14	5.936	.17ns	0.896
3.5.86	0.09192	0.01289	0.122	0.061	7.53	1.057	10.04	5.038	.20ns	0.879
6.1.86	0.07004	0.02318	0.126	0.013	9.89	3.274	17.90	1.883	0.46	0.646

B.6 Preliminary laboratory experiment on fenamiphos degradation from Dole field 4111

METHOD

This lab experiment was performed on soils collected from different locations (A to F) at Dole 4111. It was conducted in Feb. 1987 before initiation of the actual field experiment in March 1987 (see chapter 3). The purpose was to perform a trial lab experiment and to determine the effect of soils obtained from (a) inbed and (b) between beds, on degradation of fenamiphos in the lab. We suspected that the soil moisture, microbial and chemical properties may be different enough in the two sampling locations to cause a difference in the degradation of fenamiphos. Soil samples were obtained from the surface 0-15 cm depth (1) in the bed from A to F locations (designated A to F)and (2) between beds at A, C and E locations (designated AOUT, COUT AND EOUT). Standard radiolabeled fenamiphos experiments were conducted at 0.3 SMT and 23 C.

RESULTS AND DISCUSSION

The degradation half-lives of fenamiphos for inbed soil samples were relatively homogeneous: mean of 7.3 days and CV of 6% (table 21). Degradation half-lives of fenamiphos on soils obtained from between beds were slightly lower by a factor of 1.5 ($t_{0.5}$ = 5.5 days) but were not significantly different from inbed samples. Thus, there is no effect of sampling from either inbed or between beds on fenamiphos degradation.

Table 21 Preliminary study of fenamiphos degradation from Dole 4111

I.D.	K	STDERR	UPPER	LOWER	TO.5	SE	UPPER	LOWER	b	R-2
A	0.1004	0.00916	0.122	0.078	6.90	0.629	8.392	5.414	0.413	0.945
B	0.09582	0.01354	0.127	0.063	7.23	1.021	9.649	4.816	0.257ns	0.877
C	0.08959	0.00948	0.112	0.067	7.73	0.818	9.671	5.800	0.43	0.927
D	0.1004	0.01187	0.128	0.072	6.90	0.816	8.833	4.973	0.352	0.911
E	0.08720	0.01254	0.116	0.057	7.94	1.143	10.65	5.244	0.483	0.873
F	0.09892	0.01060	0.124	0.073	7.00	0.750	8.781	5.231	0.407	0.924
AOUT	0.1364	0.02010	0.183	0.088	5.08	0.748	6.852	3.310	0.61	0.868
COUT	0.1282	0.01567	0.165	0.091	5.40	0.660	6.969	3.843	0.529	0.905
EOUT	0.1182	0.01524	0.154	0.082	5.86	0.756	7.652	4.075	0.483	0.896

A TO F - SOILS OBTAINED IN BEDS
OUT - SOILS OBTAINED BETWEEN BEDS

B.7 Preliminary laboratory experiment of fen. sulfoxide degradation from Dole 4111

METHOD

Standard lab incubation experiments using radiolabeled fen. sulfoxide were conducted on soil samples collected from all locations (A to F, Dole 4111) and also on a soil sample from Maui Pine 277 (Pane silt loam, see details of soil from Appendix A.1).

RESULTS AND DISCUSSION

The mean degradation half-life of fen. sulfoxide was 47.0 days with an associated CV of 20% (table 22). These values were comparable to those obtained from lab and field experiments conducted from Del Monte field 2068 (see chapter 3, table 8). Accelerated degradation of fen. sulfoxide was found on Pane soil ($t_{0.5}$ = 30 days). The major metabolite formed was located at Rf position of 0.75 using a 3:1 ethylether/acetone solvent system. The metabolite is either fen. sulfoxide phenol or fen. sulfone phenol and is not confirmed. The major pathway of degradation on Pane soil seems to be hydrolysis and further investigations are needed on similar soil-types.

Table 22 Preliminary study of fen.sulfoxide from Dole 4111 and Maui Pine 277

I.D.	K	STDERR	UPPER	LOWER	TO.5	SE	UPPER	LOWER	b	R-2
SA	0.01882	0.00045	0.019	0.017	36.8	0.881	38.90	34.73	.006ns	0.997
SB	0.01415	0.00168	0.018	0.010	48.9	5.827	62.75	35.18	.08ns	0.959
SC	0.01242	0.00078	0.014	0.010	55.7	3.522	64.10	47.44	0.0124ns	0.988
SD	0.01823	0.00069	0.019	0.016	38.0	1.451	41.44	34.57	.006ns	0.996
SE	0.01152	0.00080	0.013	0.009	60.1	4.217	70.12	50.17	.013ns	0.986
SF	0.01639	0.00069	0.018	0.014	42.2	1.784	46.50	38.06	.025ns	0.995
PA	0.02279	0.00484	0.034	0.011	30.3	6.452	45.66	15.13	.409ns	0.847

SA TO SF - SITES A TO F FROM DOLE 4111
PA - PANE SOIL FROM MPINE 277

B.8 Standard errors and 95% confidence intervals of the degradation rate (k) and half-lives ($t_{0.5}$) of fenamiphos and fen. sulfoxide determined from laboratory and field experiments

1. Field and lab experiments of fenamiphos degradation from Dole 4111 (refer to Chapter 3 and table 5, see table 23)
2. Field and lab experiments of fenamiphos degradation from Del Monte 2068 (refer to Chapter 3 and table 6, see table 24)
3. Field and lab experiments of fen. sulfoxide degradation from Del Monte 2068 (refer to Chapter 3 and table 7, see table 25)

Table 23 Fenamiphos laboratory and degradation experiments
Dole 4111 field

I.D.	K	STDERR	UPPER	LOWER	TO.5	SE	UPPERLOWER		R2
A23	0.0937	0.013092	0.1257	0.0617	7.39	1.031	9.91	4.86	0.88
B23	0.0826	0.01516	0.1197	0.0455	8.38	1.538	12.1	4.62	0.832
C23	0.1005	0.01216	0.1302	0.0707	6.89	0.834	8.93	4.85	0.919
D23	0.0764	0.016832	0.1176	0.0352	9.06	1.996	13.9	4.18	0.775
E23	0.0880	0.01003	0.1125	0.0635	7.87	0.896	10.0	5.67	0.917
F23	0.0726	0.00974	0.0964	0.0487	9.54	1.280	12.6	6.41	0.903
A15	0.0962	0.016655	0.1370	0.0555	7.19	1.244	10.2	4.15	0.827
C15	0.0980	0.013464	0.1309	0.0650	7.07	0.970	9.44	4.69	0.883
D15	0.0674	0.013789	0.1011	0.0336	10.2	2.103	15.4	5.13	0.773
A35	0.3158	0.052771	0.4449	0.1866	2.19	0.366	3.09	1.29	0.878
C35	0.2751	0.062654	0.4284	0.1217	2.51	0.573	3.92	1.11	0.865
A	0.0615	0.008766	0.0822	0.0407	11.2	1.605	15.0	7.47	0.876
B	0.0957	0.017910	0.1380	0.0533	7.23	1.353	10.4	4.03	0.803
C	0.0713	0.014626	0.1059	0.0367	9.71	1.989	14.4	5.00	0.773
D	0.0654	0.001538	0.0690	0.0617	10.5	0.249	11.1	10.0	0.847
E	0.0944	0.007453	0.1120	0.0768	7.33	0.578	8.70	5.96	0.958
F	0.0769	0.003622	0.0855	0.0683	9.00	0.423	10.0	8.00	0.812

3,6,1- LAB SOIL MOISTURE TENSIONS 0.3, 0.6, 1.0 BAR, RESPECTIVELY
15, 23, 25 - LAB. SOIL TEMPERATURES IN CELSIUS
A TO F - FIELD SITES

Table 24 Fenamiphos laboratory and field degradation experiments
Del Monte 2068 field

I.D.	K	STDERR	UPPER	LOWER	T.5	SE	UPPER	LOWER	R2
3A23	0.154	0.009347	0.1768	0.1311	4.50	0.273	5.168	3.832	0.982
6A23	0.020023	0.053636	0.1512	-0.111	34.6	92.67	261.4	-192.	0.065
1A23	0.1399	0.004488	0.1508	0.1289	4.95	0.158	5.343	4.565	0.996
3A15	0.070032	0.008937	0.0919	0.0481	9.89	1.262	12.98	6.807	0.925
1A15	0.062022	0.004439	0.0728	0.0511	11.1	0.799	13.13	9.218	0.975
3A35	0.1642	0.034411	0.2484	0.0799	4.22	0.884	6.384	2.057	0.82
6A35	0.1652	0.033782	0.2478	0.0825	4.19	0.857	6.294	2.096	0.827
1A35	0.1839	0.024660	0.2442	0.1235	3.76	0.505	5.005	2.532	0.918
3F23	0.062278	0.005363	0.0754	0.0491	11.1	0.958	13.47	8.784	0.964
6F23	0.032806	0.008115	0.0526	0.0129	21.1	5.224	33.91	8.343	0.766
1F23	0.052348	0.003365	0.0605	0.0441	13.2	0.850	15.32	11.15	0.98
3F15	0.029527	0.003457	0.0379	0.0210	23.4	2.747	30.19	16.74	0.936
1F15	0.025635	0.001982	0.0304	0.0207	27.0	2.089	32.15	21.92	0.971
3F35	0.1181	8	0.1393	0.0968	5.86	0.430	6.923	4.814	0.974
6F35	0.072391	0.021178	0.1242	0.0205	9.57	2.799	16.42	2.723	0.745
1F35	0.085511	0.004116	0.0955	0.0754	8.10	0.389	9.059	7.150	0.989
A	0.1042	0.010476	0.1289	0.0794	6.65	0.668	8.232	5.070	0.934
B	0.1189	0.010682	0.1441	0.0936	5.82	0.523	7.067	4.591	0.947
C	0.125	0.013923	0.1579	0.0920	5.54	0.617	7.004	4.084	0.92
D	0.051709	0.020843	0.1010	0.0024	13.4	5.400	26.17	0.631	0.468
E	0.081223	0.020774	0.1303	0.0320	8.53	2.181	13.69	3.373	0.686
F	0.034278	0.007769	0.0526	0.0159	20.2	4.580	31.05	9.385	0.736
1B23	0.1471	0.008794	0.1678	0.1263	4.71	0.281	5.377	4.045	0.982
1C23	0.1541	0.011853	0.1821	0.1260	4.49	0.345	5.315	3.679	0.971
1D23	0.053541	0.011888	0.0816	0.0254	12.9	2.873	19.74	6.150	0.802
1E23	0.073630	0.008292	0.0932	0.0540	9.41	1.059	11.91	6.907	0.94

3,6,1 - LAB SOIL MOISTURE TENSIONS, 0.3, 0.6 AND 1.0 BAR, RESPECTIVELY
A TO F - FIELD SITES
15, 23, 25 - LAB. SOIL TEMPERATURES IN CELSIUS

Table 25 Fenamiphos sulfoxide laboratory and field experiments - Del Monte 2068 field

I.D.	K	STDERR	UPPER	LOWER	TO.5	SE	UPPER	LOWER	R2
3A23	0.0207	0.001140	0.0234	0.0179	33.4	1.844	37.99	28.97	0.985
6A23	0.022557	0.005752	0.0366	0.0084	30.7	7.832	49.89	11.56	0.755
1A23	0.015202	0.001675	0.0193	0.0111	45.5	5.021	57.87	33.30	0.943
3A15	0.016170	0.004499	0.0271	0.0051	42.8	11.92	72.03	13.68	0.721
1A15	0.014701	0.004771	0.0263	0.0030	47.1	15.29	84.57	9.716	0.656
3A35	0.030577	0.006873	0.0473	0.0137	22.6	5.092	35.12	10.20	0.798
6A35	0.028720	0.006995	0.0458	0.0116	24.1	5.875	38.50	9.755	0.771
1A35	0.021985	0.007107	0.0393	0.0045	31.5	10.18	56.45	6.596	0.657
3F23	0.011417	0.002929	0.0185	0.0042	60.7	15.56	98.80	22.60	0.752
6F23	0.020047	0.005872	0.0344	0.0056	34.5	10.12	59.34	9.801	0.7
1F23	0.010551	0.002162	0.0158	0.0052	65.6	13.45	98.62	32.75	0.826
3F15	0.023513	0.002947	0.0307	0.0163	29.4	3.693	38.51	20.43	0.927
1F15	0.014458	0.004590	0.0256	0.0032	47.9	15.21	85.16	10.71	0.665
3F35	0.025046	0.006614	0.0412	0.0088	27.6	7.304	45.54	9.798	0.742
6F35	0.024591	0.008691	0.0458	0.0033	28.1	9.957	52.55	3.818	0.667
1F35	0.024084	0.006266	0.0394	0.0087	28.7	7.484	47.09	10.46	0.747
A	0.013335	0.001908	0.0178	0.0088	51.9	7.436	69.56	34.38	0.875
B	0.009102	0.002006	0.0138	0.0043	76.1	16.77	115.8	36.46	0.746
C	0.01232	0.002680	0.0186	0.0059	56.2	12.23	85.19	27.32	0.751
D	0.013955	0.001538	0.0175	0.0103	49.6	5.473	62.61	36.72	0.922
E	0.016256	0.002495	0.0221	0.0103	42.6	6.541	58.10	27.16	0.859
F	0.010173	0.003622	0.0187	0.0016	68.1	24.25	125.4	10.77	0.53
1B23	0.014092	0.002448	0.0200	0.0081	49.1	8.542	70.08	28.27	0.869
1C23	0.013077	0.002027	0.0180	0.0081	52.9	8.212	73.09	32.90	0.893
1D23	0.010453	0.002653	0.0169	0.0039	66.3	16.82	107.4	25.13	0.756
1E23	0.011564	0.001989	0.0164	0.0066	59.9	10.30	85.14	34.71	0.871

3,6,1 - LAB. SOIL MOISTURE TENSIONS, 0.3, 0.6 AND 1.0 BAR, RESPECTIVELY
A TO F - FIELD SITES
15, 23, 25 - LAB. SOIL TEMPERATURES IN CELSIUS

B.9 Fraction nematicide remaining at different times for field and laboratory experiments conducted at Dole and Del Monte fields

1. Fenamiphos laboratory experiment - Dole 4111 (table 26)
2. Fenamiphos field experiment - Dole 4111 (table 27)
3. Fenamiphos laboratory experiment - Del Monte 2068 (table 28)
4. Fenamiphos field experiment - Del Monte 2068 (table 29)
5. Fen. sulfoxide laboratory experiment - Del Monte 2068 (table 30)
6. Fen. sulfoxide field experiment - Del Monte 2068 (table 31)

Table 26 Fenamiphos laboratory degradation data - Dole 4111

I.D	day	C/Co	Ln C/Co
A23	0	1	0
A23	3	0.418	-0.87227
A23	3	0.345	-1.06421
A23	7	0.214	-1.54177
A23	7	0.276	-1.28735
A23	14	0.128	-2.05572
A23	14	0.135	-2.00248
A23	21	0.096	-2.34340
A23	21	0.0943	-2.36127
B23	0	1	0
B23	3	0.519	-0.65585
B23	3	0.428	-0.84863
B23	7	0.243	-1.41469
B23	7	0.272	-1.30195
B23	14	0.194	-1.63989
B23	14	0.198	-1.61948
B23	21	0.137	-1.98777
C23	0	1	0
C23	3	0.451	-0.79628
C23	3	0.45	-0.79850
C23	7	0.34	-1.07880
C23	7	0.313	-1.16155
C23	14	0.134	-2.00991
C23	14	0.154	-1.87080
C23	21	0.11	-2.20727
D23	0	1	0
D23	3	0.478	-0.73814
D23	3	0.346	-1.06131
D23	7	0.235	-1.44816
D23	7	0.284	-1.25878
D23	14	0.203	-1.59454
D23	14	0.184	-1.69281
D23	21	0.145	-1.93102
E23	0	1	0
E23	3	0.451	-0.79628
E23	3	0.521	-0.65200
E23	7	0.31	-1.17118
E23	7	0.336	-1.09064
E23	14	0.149	-1.90380
E23	14	0.183	-1.69826
E23	21	0.127	-2.06356
E23	21	0.124	-2.08747

Table 26 continued

I.D	day	C/Co	Ln C/Co
F23	0	1	0
F23	3	0.492	-0.70927
F23	3	0.574	-0.55512
F23	7	0.327	-1.11779
F23	7	0.337	-1.08767
F23	14	0.244	-1.41058
F23	21	0.162	-1.82015
F23	21	0.165	-1.80180

Table 27 Fenamiphos field degradation data - Dole 4111

I.D	day	C/Co	Ln C/Co
A	0	1	0
A	3	0.56	-0.57981
A	3	0.55	-0.59783
A	7	0.38	-0.96758
A	7	0.42	-0.86750
A	14	0.36	-1.02165
A	14	0.27	-1.30933
A	21	0.18	-1.71479
A	21	0.24	-1.42711
B	0	1	0
B	3	0.73	-0.31471
B	3	0.86	-0.15082
B	7	0.395	-0.92886
B	7	0.27	-1.30933
B	14	0.19	-1.66073
B	14	0.15	-1.89711
B	21	0.23	-1.46967
B	21	0.09	-2.40794
C	0	1	0
C	3	0.5	-0.69314
C	3	0.81	-0.21072
C	7	0.3	-1.20397
C	7	0.3	-1.20397
C	14	0.3	-1.20397
C	14	0.18	-1.71479
C	21	0.195	-1.63475
C	21	0.18	-1.71479
D	0	1	0
D	3	0.58	-0.54472
D	3	0.48	-0.73396
D	7	0.32	-1.13943
D	7	0.35	-1.04982
D	14	0.25	-1.38629
D	14	0.22	-1.51412
D	21	0.2	-1.60943
D	21	0.19	-1.66073
E	0	1	0
E	3	0.74	-0.30110
E	3	0.67	-0.40047
E	7	0.33	-1.10866
E	7	0.45	-0.79850
E	14	0.22	-1.51412
E	14	0.24	-1.42711
E	21	0.11	-2.20727
E	21	0.15	-1.89711

Table 27 continued

I.D	day	C/Co	Ln C/Co
F	0	1	0
F	3	0.715	-0.33547
F	3	0.8	-0.22314
F	7	0.535	-0.62548
F	7	0.39	-0.94160
F	14	0.29	-1.23787
F	14	0.35	-1.04982
F	21	0.31	-1.17118
F	21	0.11	-2.20727

Table 28 Fenamiphos laboratory degradation data - Del Monte 2068

I.D.	day	C/Co	Ln C/Co
1A23	0	1	0
1A23	3	0.565	-0.57017
1A23	7	0.337	-1.08516
1A23	7	0.353	-1.03888
1A23	14	0.133	-2.01403
1A23	14	0.132	-2.02077
1B23	0	1	0
1B23	3	0.511	-0.67018
1B23	3	0.473	-0.74800
1B23	7	0.283	-1.26151
1B23	7	0.282	-1.26547
1B23	14	0.118	-2.13062
1B23	14	0.103	-2.26720
1C23	0	1	0
1C23	3	0.467	-0.76117
1C23	3	0.445	-0.80845
1C23	7	0.221	-1.50551
1C23	7	0.264	-1.32929
1C23	14	0.104	-2.26214
1C23	14	0.091	-2.38825
1D23	0	1	0
1D23	3	0.619	-0.47912
1D23	3	0.702	-0.35254
1D23	7	0.508	-0.67550
1D23	7	0.447	-0.80498
1D23	14	0.424	-0.85788
1D23	14	0.405	-0.90227
1E23	0	1	0
1E23	3	0.744	-0.29541
1E23	3	0.700	-0.35623
1E23	7	0.465	-0.76501
1E23	7	0.463	-0.76854
1E23	14	0.346	-1.06002
1E23	14	0.331	-1.10490
1F23	0	1	0
1F23	3	0.803	-0.21933
1F23	3	0.781	-0.24717
1F23	7	0.665	-0.40727
1F23	7	0.715	-0.33504
1F23	14	0.469	-0.75653
1F23	14	0.453	-0.79135

Table 29 Fenamiphos field degradation data
Del Monte 2068

I.D	day	C/Co	Ln C/Co
A	0	1	0
A	3	0.657	-0.42007
A	3	0.768	-0.26396
A	7	0.333	-1.09961
A	7	0.407	-0.89894
A	14	0.228	-1.47840
A	14	0.328	-1.11474
A	21	0.08	-2.52572
A	21	0.116	-2.15416
B	0	1	0
B	3	0.674	-0.39452
B	3	0.464	-0.76787
B	7	0.408	-0.89648
B	7	0.316	-1.15201
B	14	0.194	-1.63989
B	14	0.103	-2.27302
B	21	0.07	-2.65926
B	21	0.081	-2.51330
C	0	1	0
C	3	0.68	-0.38566
C	3	0.5	-0.69314
C	7	0.507	-0.67924
C	7	0.701	-0.35524
C	14	0.138	-1.98050
C	14	0.115	-2.16282
C	21	0.086	-2.45340
C	21	0.076	-2.57702
D	0	1	0
D	3	0.542	-0.61248
D	3	0.377	-0.97551
D	7	0.21	-1.56064
D	7	0.28	-1.27296
D	14	0.144	-1.93794
D	14	0.305	-1.18744
D	21	0.175	-1.74296
D	21	0.299	-1.20731
E	0	1	0
E	3	0.913	-0.09101
E	3	0.82	-0.19845
E	7	0.416	-0.87707
E	7	0.416	-0.87707
E	14	0.744	-0.29571
E	14	0.206	-1.57987
E	21	0.251	-1.38230
E	21	0.109	-2.21640

Table 29 continued

I.D	day	C/Co	Ln C/Co
F	0	1	0
F	3	0.847	-0.16605
F	3	0.83	-0.18632
F	7	0.665	-0.40796
F	7	0.727	-0.31882
F	14	0.868	-0.14156
F	14	0.581	-0.54300
F	21	0.382	-0.96233
F	21	0.478	-0.73814

Table 30 Fenamiphos sulfoxide laboratory degradation data
Del Monte 2068

I.D	days	C/Co	Ln C/Co
1A23	0	1	0
1A23	14	0.74695	-0.2917
1A23	14	0.75691	-0.2785
1A23	35	0.48187	-0.7300
1A23	35	0.49496	-0.7032
1A23	56	0.43046	-0.8428
1A23	56	0.41532	-0.8786
1B23	0	1	0
1B23	14	0.89684	-0.1088
1B23	14	0.76032	-0.2740
1B23	35	0.54326	-0.6101
1B23	35	0.48263	-0.7284
1B23	56	0.50393	-0.6853
1B23	56	0.44095	-0.8188
1C23	0	1	0
1C23	14	0.87977	-0.1280
1C23	14	0.81831	-0.2005
1C23	35	0.52793	-0.6387
1C23	35	0.54513	-0.6067
1C23	56	0.51875	-0.6563
1C23	56	0.48539	-0.7227
1D23	0	1	0
1D23	14	0.71178	-0.3399
1D23	14	0.64870	-0.4327
1D23	35	0.52518	-0.6440
1D23	35	0.51109	-0.6712
1D23	56	0.553	-0.592
1D23	56	0.467	-0.761
1E23	0	1	0
1E23	14	0.67580	-0.3918
1E23	14	0.71162	-0.3402
1E23	35	0.51809	-0.6576
1E23	35	0.53252	-0.6301
1E23	56	0.486	-0.722
1E23	56	0.481	-0.732
1F23	0	1	0
1F23	14	0.79377	-0.2309
1F23	14	0.80495	-0.2169
1F23	35	0.55588	-0.5871
1F23	35	0.54504	-0.6068
1F23	56	0.52778	-0.6390
1F23	56	0.57785	-0.5484

Table 31 Fenamiphos field degradation data
Del Monte 2068

I.D	day	C/Co	Ln C/Co
A	0	1	0
A	14	0.64	-0.446
A	14	0.696	-0.362
A	30	0.509	-0.675
A	30	0.667	-0.404
A	43	0.515	-0.663
A	43	0.502	-0.689
A	56	0.401	-0.913
A	56	0.438	-0.825
B	0	1	0
B	14	0.709	-0.343
B	14	0.833	-0.182
B	30	0.777	-0.252
B	30	0.689	-0.372
B	43	0.514	-0.665
B	43	0.656	-0.421
B	56	0.551	-0.596
B	56	0.614	-0.487
C	0	1	0
C	14	0.729	-0.316
C	14	0.729	-0.316
C	30	0.599	-0.512
C	30	0.523	-0.648
C	43	0.416	-0.877
C	43	0.447	-0.805
C	56	0.526	-0.642
C	56	0.501	-0.691
D	0	1	0
D	14	0.633	-0.457
D	14	0.637	-0.450
D	30	0.593	-0.522
D	30	0.548	-0.601
D	43	0.487	-0.719
D	43	0.47	-0.755
D	56	0.405	-0.903
D	56	0.393	-0.933
E	0	1	0
E	14	0.782	-0.245
E	14	0.764	-0.269
E	30	0.739	-0.302
E	30	0.505	-0.683
E	43	0.44	-0.820
E	43	0.4	-0.916
E	56	0.434	-0.834
E	56	0.417	-0.874

Table 31 continued

I.D	day	C/Co	Ln C/Co
F	0	1	0
F	14	0.823	-0.194
F	14	0.634	-0.455
F	30	0.643	-0.441
F	30	0.548	-0.601
F	43	0.564	-0.572
F	43	0.377	-0.975
F	56	0.596	-0.517
F	56	0.543	-0.610

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